and 1.82 (3) Å for the tin and lead compounds, respectively) are among the longest recorded (see Table III), and the shorter (d(C—S) values (1.702 (11) and 1.67 (3) Å for the tin and lead compounds, respectively) are among the shortest, as would be expected for a monodentate ligand.

Additional assurance that the four-coordinated geometry is correct comes from the bonded d(Sn–S) value which at 2.468 (3) Å is below the 2.48 Å average of values drawn from the monodentate (dithiocarbamato)tin(IV) determinations and is much smaller than the 2.67 Å average value of the chelated systems. Unfortunately, since ours is the first such determination for a lead(IV) derivative, no comparisons of this kind are possible.

There is no incipient bridging of the ligands in the title compounds. All intermolecular M···S distances are greater than 4.5 Å. The intramolecular S···S distances are 2.986 (3) and 3.009 (15) Å in I and II, respectively. The least-squares planes are listed in Table SVI. The metal–S_2CN systems are quite planar, with the pyrrole rings twisted out of this plane by 8.30–9.96°.

The contiguous d(C–N) values in both title compounds are among the shortest recorded (see Table III). In the valence bond model discussed above, this would be expected to lead to long carbon–sulfur distances and coplanarity for the S_2C and NC_2 systems. The d(C–S) values we record do not seem particularly short, however. Replacing tin(IV) by lead(IV) in the title compound results in an expansion of the metal–sulfur ester bond by 0.09 or 3.7%, and the nonbonded metal–sulfur contact by 0.154 or 5%, but the bonds to the phenyl groups expand by only 0.04 Å or 1.9%.

Acknowledgment. Our work is supported by the Office of Naval Research (J.J.Z.).

Registry No. I, 26879-86-7; II, 97210-85-0; $(C_2H_5)_3GeL$, 97190-96-0; $(CH_3)_2SnL_2$, 26122-22-5; $(C_2H_5)_2SnL_2$, 97190-97-1; $(n\text{-}C_4H_9)_2SnL_2$, 22381-90-4; $(n\text{-}C_8H_{17})_2SnL_2$, 73160-43-7; $(C_6H_5)_2SnL_2$, 22484-01-1; $[NH_4]^+[S_2CN(CH_2)_4]^-$, 5108-96-3; $(C_2H_5)_3GeCl$, 994-28-5; $(CH_3)_2SnCl_2$, 753-73-1; Ph_2SnCl_2, 1135-99-5; $(C_2H_5)_2SnCl_2$, 866-55-7; $(n\text{-}C_4H_9)_2SnCl_2$, 683-18-1; $(n\text{-}C_8H_{17})_2SnCl_2$, 3542-36-7; Ph_3SnCl, 639-58-7; Ph_3PbCl, 1153-06-6.

Supplementary Material Available: Tables of mass spectral data for the R_3ML (Table SI) and R_2ML_2 (Table SII) derivatives, infrared frequencies for the di- (Table SIII) and triorgano (Table SIV) derivatives, Raman frequencies (Table SV), the calculation of planes for I and II (Table SVI), the anisotropic thermal parameters for I (Table SVII) and II (Table SVIII), and structure factors (64 pages). Ordering information is given on any current masthead page.

Synthesis and Reaction of (η^3-1-Methyl-1-(trimethylsilyl)allyl)(μ-dichloro)dipalladium(II). Molecular Structure of *anti*-(η^3-1-Methyl-1-(trimethylsilyl)allyl)chloro(triphenylphosphine)palladium(II)

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The reaction of trimethylvinylsilane with $PdCl_2$ in DME in the presence of MeOH at room temperature produces *syn*-(η^3-1-methyl-1-(trimethylsilyl)allyl)(μ-dichloro)dipalladium(II) (1). The anti complex 2 was obtained by heating 1 in $CHCl_3$ at 60 °C. Structural elucidation of syn and anti complexes 1 and 2 has been made by the NMR studies, including Overhauser experiments. X-ray crystallography of the *anti*-(η^3-1-methyl-1(trimethylsilyl)allyl)chloro(triphenylphosphine)palladium(II) (4) confirms the anti structure. The mechanism and stereochemical course for the formation of 1 and 2 are described briefly. The reactions of the π-allyl complexes 1 and 2 with sodium malonate give (E)-ethyl 5-(trimethylsilyl)-2-carbethoxy-4-hexenoate (**15**) and its Z isomer (**16**), respectively. Similarly, the reactions with N-methylaniline give [(E)-(and (Z))-1-methyl-3-(methylphenylamino)-1-propenyl]trimethylsilane (17 and 18) regio- and stereoselectively.

Introduction

Weber et al. reported that the reaction of $(CH_3)_3SiCH{=}CHPh$ with $PdCl_2$ gave 1,4-diphenyl-1,3-butadiene via vinylpalladium(II) intermediate arising from Pd(II)-induced desilylation.[1] Recently, metal-induced desilylations have been documented for the arylation of vinylsilanes with $[ArPd]^+X^-$[2] and the vinylation of alkenes with $[RCH{=}CHSiF_5]K_2$ and Pd(II) salts.[3] Yamamoto et al. have reported that silylated (π-allyl)palladium complexes are prepared by the reaction of $(CH_3)_3SiCH{=}CH_2$

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[1] Weber, W. P.; Felix, R. A.; Willard, A. K.; Koening, K. E. *Tetrahedron Lett.* **1971**, 4701.

[2] Kikukawa, K.; Ikenaga, K.; Kono, K.; Toritani, K.; Wada, F.; Matsuda, T. *J. Organomet. Chem.* **1984**, *270*, 277; see also; Hallberg, A.; Westerlund, C. *Chem. Lett.* **1982**, 1993.

[3] Yoshida, J.; Tamao, K.; Yamamoto, H.; Kakui, T.; Uchida, T.; Kumada, M. *Organometallics* **1982**, *1*, 542.

Table I. Formation of (π-Allyl)palladium(II) Complexes 1 and 2[a]

entry	ratio of $PdCl_2$/TMVS[d]/MeOH	temp, °C	time, h	yield,[b] %	isomer[c] ratio
1	1/4/4	50	20	91	50/50
2	1/4/4	50	74	84	18/82
3	1/4/4	rt	20	92	100/0
4	1/4/0	rt	200	58	100/0

[a] Reactions were performed by using $PdCl_2$ (0.5 mmol), vinylsilane (2 mmol), MeOH (2 mmol), and DME (2 mL) under Ar. [b] Isolated yield based on Pd. [c] Determined by NMR analysis. [d] TMVS = trimethylvinylsilane.

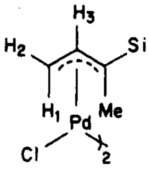
Table II. Nuclear Overhauser Effects in the Complexes 1 and 2[a]

Pd complex	intensity increase (%) H_1	H_2	H_3
	Irradiation at the Me Signal		
1	9.8	2.8	4.7
2	0.6	0.6	10
	Irradiation at the $SiMe_3$ Signal		
1	0.9	2.1	3.7
2	10	3.3	4.5

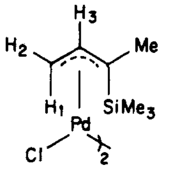
[a] Details are described in the Experimental Section.

with $PdCl_2$ $(CH_3CN)_2$ via dimerization of vinylsilane.[4] This type of silylated (π-allyl)palladium complexes have been prepared from the reactions of $(CH_3)_3SiCH{=}CHCH_2Cl$[5] and $(CH_3)_3SiCH{=}CHCH_2Si(CH_3)_3$[6] with palladium(II) salts.

We have found that the reaction of $(CH_3)_3SiCH{=}CH_2$ with $PdCl_2$ in the presence of methanol gives *syn*- and *anti*-(η^3-1-methyl-1-(trimethylsilyl)allyl)(μ-dichloro)dipalladium(II) (1 and 2). Each of the pure stereoisomers can be prepared simply by changing the reaction temperature. Structural elucidation of 1 and 2 by the aid of NMR spectroscopy and X-ray crystallography and their stereoselective transformations to synthetically useful substituted vinylsilanes[7] are reported here.



syn-1



anti-2

Results and Discussion

1. Preparation of Silylated (π-Allyl)palladium(II) Complexes. When vinyltrimethylsilane was allowed to react with $PdCl_2$ in 1,2-dimethoxyethane (DME) in the presence of methanol at 50 °C,[8] a 50:50 mixture of complexes 1 and 2 was obtained in 91% yield. Prolonged reaction time at 50 °C gave an 18:82 mixture of 1 and 2 (Table I, entry 2). Use of lower reaction temperature gave only the syn complex 1 (entry 3). In the absence of methanol, the rate of product formation was extremely slow (entry 4). The syn complex 1 in $CHCl_3$ was isomerized into the anti complex 2 upon heating at 60 °C.

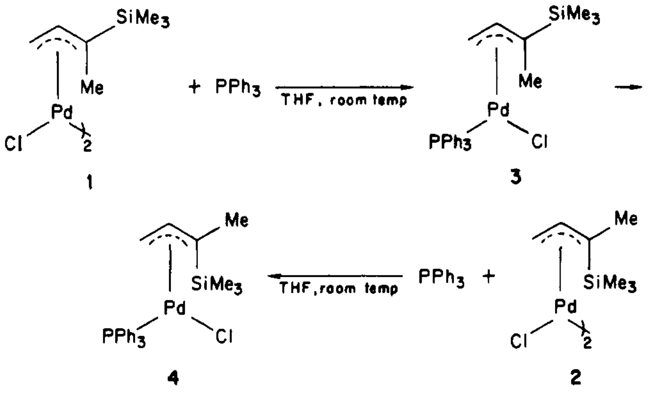
Table III. Selected Bond Distance (Å) for Complex 4

Pd-Cl	2.372 (1)	C(1)-C(2)	1.402 (5)
Pd-P	2.311 (1)	C(2)-C(3)	1.391 (5)
Pd-C (1)	2.116 (4)	C(3)-C(4)	1.527 (6)
Pd-C(2)	2.154 (4)	C(3)-Si	1.897 (4)
Pd-C(3)	2.240 (4)	Si-C(5)	1.869 (5)
P-C(11)	1.826 (4)	Si-C(6)	1.864 (5)
P-C(21)	1.834 (4)	Si-C(7)	1.863 (5)
P-C(31)	1.824 (3)		

Table IV. Selected Bond Angles (deg) for Complex 4

Cl-Pd-P	99.60 (3)	Pd-C(3)-C(4)	118.2 (3)
P-Pd-C(1)	97.87 (10)	Pd-C(3)-Si	103.32 (15)
Cl-Pd-C(3)	94.45 (9)	Pd-C(3)-C(2)	68.2 (2)
C(1)-Pd-C(3)	68.21 (13)	C(2)-C(3)-Si	126.2 (3)
Pd-P-C(11)	115.75 (11)	C(4)-C(3)-Si	114.1 (3)
Pd-P-C(21)	113.28 (10)	C(2)-C(3)-C(4)	116.1 (4)
Pd-P-C(31)	113.53 (10)	C(3)-Si-C(5)	115.62 (18)
C(11)-P-C(21)	104.32 (14)	C(3)-Si-C(6)	105.73 (18)
C(11)-P-C(31)	103.92 (14)	C(3)-Si-C(7)	107.81 (18)
C(21)-P-C(31)	104.87 (14)	C(5)-Si-C(6)	109.6 (2)
Pd-C(1)-C(2)	72.3 (3)	C(5)-Si-C(7)	108.0 (2)
C(1)-C(2)-C(3)	122.1 (4)	C(6)-Si-C(7)	110.0 (2)

Treatment of 1 and 2 with triphenylphosphine (1.0 equiv) gave the phosphine complexes 3 and 4, respectively. Complex 3 could be isomerized to 4 by heating it in $CHCl_3$ at 60 °C. The Pd acetate analogues of complexes 1 and 2 (5 and 6) were prepared by the reaction 1 and 2 with AgOAc in $CHCl_3$.



2. NMR Spectroscopic Study. The ^1H NMR spectra of complexes 1 and 2 show three sets of resonances corresponding to π-allylic protons at δ 3.40, 4.02, and 5.17 and at δ 2.96, 3.73, and 5.54, respectively. Generally, the protons which are closer to palladium appear at higher field. The Me proton signal of syn isomer 1 appears at higher field (δ 1.11) than that of *anti*-2 (δ 1.35), suggesting that the complex 1 has syn configuration with respect to $SiMe_3$ group. This result is in conflict with the observation that the $SiMe_3$ signal in complex 1 appears at higher field (δ 0.22) than that in complex 2 (δ 0.26). Therefore, we investigated the nuclear Overhauser effect for complexes 1 and 2. The results are given in Table II. Irradiation of the Me signal of complex 1 induces the highest enhancement (9.8%) of the resonance due to the H_1 proton, whereas that of complex 2 induces only 0.6% enhancement. In the case of complex 2, the highest enhancement (10%) is observed at the central proton H_3, indicating that the Me group is close to the H_3 proton. Accordingly, 2 must have the anti configuration with respect to the $SiMe_3$ group. Irradiation of the $SiMe_3$ signal of complex 2 induces

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[4] Yamamoto, K.; Shinohara, K.; Ohuchi, T.; Kumada, M. *Tetrahedron Lett.* **1974**, 1153.

[5] Pannell, K. H.; Lappert, M. F.; Stanley, K. *J. Organomet. Chem.* **1976**, *112*, 37.

[6] Corriu, R. J. P.; Escudié, N.; Guerin, C. *J. Organomet. Chem.* **1984**, *271*, C7.

[7] (a) Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: Berlin, 1983. (b) Colvin, E. "Silicon in Organic Synthesis"; Butterworths: London 1981. (c) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761.

[8] Hosokawa, T.; Ohta, T.; Murahashi, S.-I. *J. Chem. Soc., Chem. Commun.* **1983**, 848.

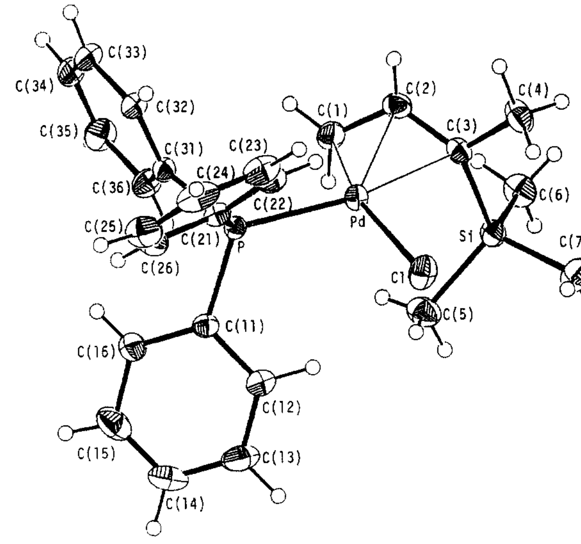


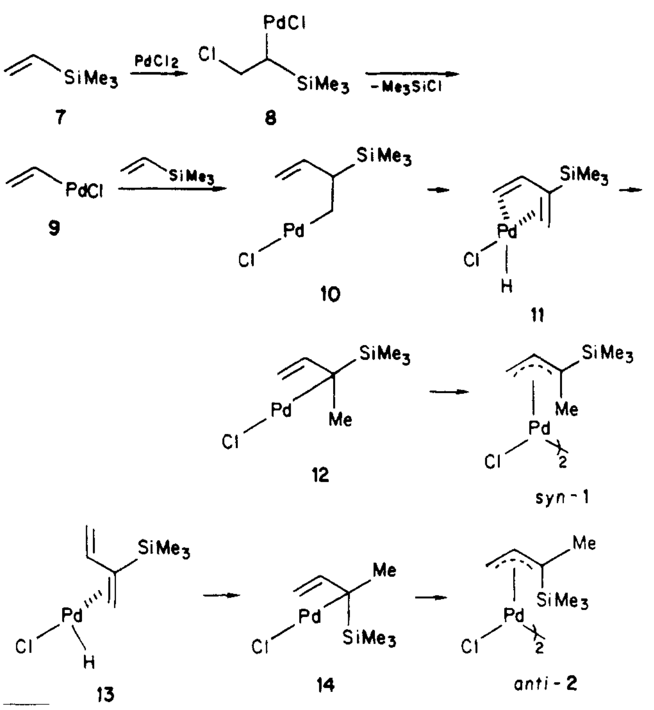
Figure 1. A perspective view of the molecular structure of 4 (an ORTEP drawing[9]) with atomic numbering systems. Non-hydrogen atoms are represented by thermal ellipsoids at 30% probability levels, whereas temperature factors of hydrogens are arbitrarily reduced for clarity.

the highest enhancement (10%) of the H_1 proton, whereas irradiation of that of complex 1 induces only 0.9% enhancement. This observation also agrees well with the structural assignments of 1 and 2.

3. Structural Elucidation of 4 by X-ray Crystallography. The conclusive evidence for the structure of the silylated (π-allyl)palladium complexes has been obtained from X-ray structure analysis. The crystals suitable for the X-ray diffraction study could not be obtained from 1 and 2 but were obtained from the phosphine complex 4.

A perspective view of the molecular structure of (η^3-1-methyl-1-(trimethylsilyl)allyl)chloro(triphenylphosphine)palladium(II) (4) is shown in Figure 1.[9] Selected bond distances and angles are listed in Tables III and IV, respectively. The geometry around the Pd atom is square planar. In the π-allyl group, the C(1)–C(2) and C(2)–C(3) bond distances (1.402 (5) and 1.391 (5) Å), which are almost equal to each other, are the expected values for C–C bonds in a π-allyl group. However, the Pd–C(3) distance (trans to P) of 2.240 (4) Å is significantly longer than the Pd–C(1) distance (trans to Cl) of 2.116 (4) Å, which is probably due to the trans influence of the PPh_3 ligand.[10] In the present complex, the π-allyl plane defined by the C(1), C(2), and C(3) atoms inclines at 117.4° to the coordination plane defined by the Pd, Cl, and P atoms. This angle is slightly greater than that in the typical unsubstituted (π-allyl)palladium complex $[(\pi\text{-}C_3H_5)PdCl]_2$[11] (111.5°) but falls in the range between 95 and 125° found in the (π-allyl)palladium complexes.[12] The present X-ray crystallography established that the $SiMe_3$ group of the thermodynamically stable product 4 is located in the anti position with respect to the central H_3 hydrogen atom of the π-allyl group, as is expected from the Overhauser experiment. This result could be extended to the configuration of the complex 2 which is also thermodynamically stable.

Scheme I



The reaction of substituted alkenes and allylic compounds with palladium chloride have been known to produce π-allyl complexes with the bulkiest substituent in the syn position.[13] The thermodynamic stability of π-allyl complexes is dependent on the steric hindrance between the Pd atom and the substituent in the anti position. Therefore, the steric hindrance between the Pd atom and the anti Me group in complex 1 (or 3) seems to be larger than that between Pd and the anti $SiMe_3$ group in complex 2 (or 4), since the latter complex is the thermodynamically stable product in the present reaction. In complex 4, the Si atom position deviates by 0.94 Å from the π-allyl plane to the opposite direction of the Pd, while C(4) atom by 0.36 Å to the direction of Pd. Further, the bond angle of C(3)–Si–C(5) (115.6°) is somewhat larger than the other two angles of C(3)–Si–C(6) (105.7°) and C(3)–Si–C(7) (107.8°). These facts indicate that the anti $SiMe_3$ group suffers steric interference to some extent. However, the $SiMe_3$ group can be accommodated in the anti position, because the Si–C(3) bond distance (1.897 Å) is much larger than the C(3)–C(4) bond distance (1.527 Å). Further, rehydridization of the carbon atoms enhances interaction between allyl ligand and palladium atom.[14]

5. Mechanism. According to Weber's proposed mechanism[2] the formation of 1 could be envisioned by Scheme I. Chloropalladation of the vinylsilane with $PdCl_2$ (7) followed by elimination of Me_3SiCl gives vinylpalladium species 9.[15] Insertion of the vinylsilane into 9 affords the σ-palladium(II) complex 10 which undergoes β-hydride elimination to give the (diene)PdHCl species 11. Cis addition of Pd–H to the diene in the direction opposite to its elimination results in the formation of π-allyl complex 1. The syn isomer 1 would be produced, if the addition of Pd–H to the coordinated diene proceeds from the cisoid form like 11 (Scheme I). On the other hand, the transoid

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[9] Johnson, C. K. ORTEP-II, Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

[10] (a) Pidcock, A.; Richards, R. E.; Venanzi, I. M. *J. Chem. Soc. A* **1966**, 1707. (b) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

[11] Smith, A. E. *Acta Crystallogr.* **1965**, *18*, 331.

[12] Hartley, F. R. "The Chemistry of Platinum and Palladium"; Applied Science: London, 1973.

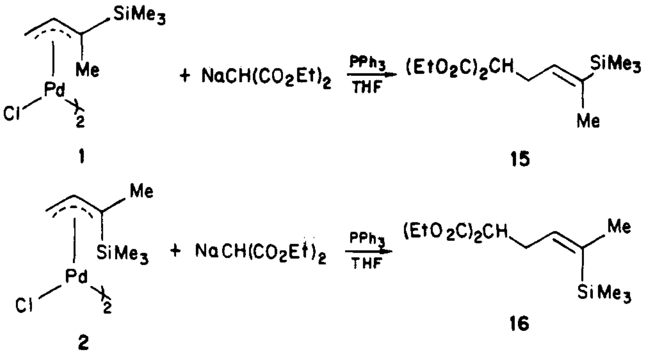
[13] (a)Lukas, J.; Ramakers-Blom, J. E.; Hewitt, T. G.; De Boer, J. J. *J. Organomet. Chem.* **1972**, *46*, 167. (b) Lukas, J.; Coren, S.; Blom, J. E. *J. Chem. Soc., Chem. Commun.* **1969**, 1303.

[14] Goddard, R.; Krüger, C.; Mark, F.; Stansfield, R.; Zhang, X. *Organometallics* **1985**, *4*, 285.

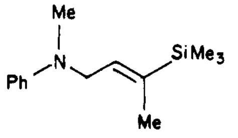
[15] As for vinylpalladium(II), see: Murahashi, S.-I.; Yamamura, M.; Yanagisawa, K.; Mita, N.; Kondo, K. *J. Org. Chem.* **1979**, *44*, 2408.

(diene)PdHCl species **13** would give the anti isomer **2**. Since dienes generally prefer to coordinate to metals as the cisoid form,[16] the syn isomer **1** seems to be formed preferentially as the kinetic product. The thermal isomerization of the syn complex **1** to the anti **2** proceeds by usual π–α–π rearrangements.[17]

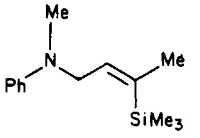
6. Reactions. It is well-known that (π-allyl)palladium(II) complexes react with various nucleophiles in the presence of phosphine ligand to give allylic compounds.[18] When each of the stereoisomers **1** and **2** was treated with diethyl sodiomalonate in the presence of 4 equiv of PPh_3 in THF at room temperature, nucleophilic attack occurred at the less crowded C_1 carbon in the usual manner. The syn isomer **1** gave only (E)-vinylsilane **15** in 60% isolated yield, whereas the anti isomer **2** afforded **16** in 79% yield stereospecifically. The stereochemistry of vinylsilanes **15** and **16** was unambiguously determined according to the Chan's NMR spectral assignment.[19] The vinyl proton (δ 5.62) and methyl protons (δ 0.04) of $SiMe_3$ group in **15** appear at higher field than those (δ 5.85 and 0.14) of **16**. Thus, (E)- and (Z)-vinylsilanes can be prepared stereospecifically. It is noteworthy that (E)-vinylsilanes have been prepared by palladium-induced alkylation of (trimethylsilyl)allyl



The palladium-catalyzed amination[21] of syn complex **1** with N-methylaniline gave (E)-vinylsilane **17** in 83% yield. On the other hand, the anti complex **2** afforded the corresponding Z isomer **18** in 46% yield. These results indicate that a variety of vinylsilanes can be prepared stereoselectively using these π-allyl complexes.



17



18

Experimental Section

General Data. NMR spectra were recorded on a 60-MHz JNM-MH-60 (JEOL) or PMX-60 SI (JEOL) and a 100-MHz JMN-FX-100 (JEOL) spectrometer; chemical shifts (δ) were expressed in parts per million relative to tetramethylsilane. IR spectra were recorded on a Hitachi 215 spectrometer. GLC for analysis was carried out on a JEOL Model JGC-20-KFP (flame ionization chromatography) using a 1 m × 1 mm, 10% PEG 20 M on 80–120 mesh Uniport HP under the condition of an injection temperature equal to 200 °C.

Trimethylvinylsilane (Shin-Etsu Silicon Chemicals) and diethyl malonate (Tokyo Kasei Kogyo Co., Ltd.) are commercially available.

***syn*-(η^3-1-Methyl-1-(trimethylsilyl)allyl)(μ-dichloro)dipalladium(II) (1).** In a 100-mL round bottomed flask was placed $PdCl_2$ (2.660 g, 15 mmol), trimethylvinylsilane (6.014 g, 60 mmol), methanol (1.922 g, 60 mmol), and DME (40 mL). The resulting heterogeneous solution was stirred for 20 h at room temperature under argon. The reaction mixture gradually turned into a clean, yellow solution, along with the precipitation of a small amount of metal. Filtration followed by concentration in vacuo afforded pure (η^3-1-methyl-1-(trimethylsilyl)allyl)(μ-dichloro)dipalladium(II) (1) (3.170 g, 92% yield): mp 165–167 °C dec; R_f 0.41 (SiO_2, ethyl acetate/hexane = 1:9); IR (Nujol) 1248, 923, 842 cm^{-1}. Anal. Calcd for $C_7H_{15}ClPdSi$: C, 31.24; H, 5.62; Cl, 13.17. Found: C, 31.11; H, 5.62; Cl, 13.10. Complex **1** is identical with that obtained from the reaction of vinylsilane with $PdCl_2(PhCN)_2$ as reported by Yamamoto.[4] Table I shows the results for other variations of the reaction conditions. The ^1H NMR spectral data of complex **1** are listed in Table III together with those of complexes **2–4** described below.

***anti*-(η^3-Methyl-1-(trimethylsilyl)allyl)(μ-dichloro)dipalladium(II) (2).** Complex **1** (2.000 g, 7.4 mmol) was stirred at 60 °C in $CHCl_3$ (60 mL) for 72 h. Removal of the solvent gave a yellow solid consisting of an 18:82 mixture of **1** and **2**, as determined by ^1H NMR spectroscopy. Repeated recrystallization of this mixture from $CHCl_3$ afforded the pure complex **2** (0.873 g, 0.32 mmol) in 44% yield: mp 168 °C dec; IR (Nujol) 1262, 1249, 914, 840, 759 cm^{-1}. Anal. Calcd for $C_7H_{15}ClPdSi$: C, 31.24; H, 5.62; Cl, 13.17. Found: C, 30.96; H, 5.56; Cl, 13.37.

***syn*-(η^3-1-Methyl-1-(trimethylsilyl)allyl)chloro(triphenylphosphine)palladium(II) (3).** A mixture of (π-allyl)palladium(II) complex **1** (0.081 g, 0.3 mmol) and triphenylphosphine (0.079 g, 0.3 mmol) in THF (3 mL) was stirred at room temperature for 1 h. Concentration of the mixture under reduced pressure followed by preparative TLC on silica gel (R_f 0.53, ethyl acetate/hexane = 3:7) gave **3** in 72% yield: mp 118 °C dec; IR (Nujol) 1250, 1100, 1002, 930, 845, 795 cm^{-1}. Anal. Calcd for $C_{25}H_{30}ClPPdSi$: C, 56.50; H, 5.69. Found: C, 56.52; H, 5.68.

***anti*-(η^3-1-Methyl-1-(trimethylsilyl)allyl)chloro(triphenylphosphine)palladium(II) (4).** Complex **4** was prepared by the same manner as above in 87% yield: mp 151–152 °C dec; IR (Nujol) 1342, 1094, 918, 832, 740, 688 cm^{-1}. Anal. Calcd for $C_{25}H_{30}ClPPdSi$: C, 56.50; H, 5.69. Found C, 56.38; H, 5.68.

***syn*-(η^3-1-Methyl-1-(trimethylsilyl)allyl)(μ-diacetato)dipalladium(II) (5).** A mixture of *syn*-**1** (0.269 g, 1 mmol) and AgOAc (0.167 g, 1 mmol) in chloroform (10 mL) was stirred at room temperature for 30 min, and the resulting AgCl was filtered. Concentration of the filtrate in vacuo gave **5** in 86% yield: mp 81.5–83 °C dec; IR (Nujol) 1570 (C=O), 1252, 1120, 915, 840, 718 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.23 (s, 9 H, $SiMe_3$), 1.18 (s, 3 H, CH_3), 2.00 (s, 3 H, $C(O)CH_3$), 3.33 (d, J = 12 Hz, 1 H, $=CH_2$), 3.91 (d, J = 7 Hz, 1 H, $=CH_2$), 5.34 (dd, J = 7, 12 Hz, 1 H, =CH).

***anti*-(η^3-1-Methyl-1-(trimethylsilyl)allyl)(μ-diacetato)dipalladium(II) (6).** Complex **6** was prepared in the same manner in 80% yield: mp 111–112 °C dec; very soluble even in pentane; IR (Nujol) 1575 (C=O), 1250, 1118, 912, 846, 716 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.30 (s, 9 H, $SiMe_3$), 1.17 (s, 3 H, CH_3), 2.00 (s, 3 H, $C(O)CH_3$), 2.95 (d, J = 12 Hz, 1 H, $=CH_2$), 3.53 (d, J = 7 Hz, 1 H, $=CH_2$), 5.46 (dd, J = 7, 12 Hz, 1 H, =CH).

Thermal Isomerization of Syn Complexes 1 and 3 into Anti Complexes 2 and 4. The syn complex **1** (0.173 g, 0.65 mmol) was heated at 60 °C in chloroform (5 mL) with stirring. After 40 h, removal of the solvent gave an 18:82 mixture of complexes **1** and **2** (by NMR). Recrystallization from chloroform gave pure *anti*-**2** (0.036 g, 21%).

Similarly, heating the complex **3** (0.159 g, 0.3 mmol) in chloroform (5 mL) at 60 °C gave a 13:87 mixture of **3** and **4**. Pure **4** (0.048 g, 30%) was isolated by recrystallization from chloroform.

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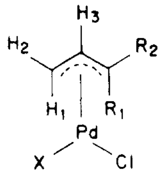
Table V. ^{1}H NMR Spectra Data for (π-Allyl)palladium Complexes 1–4[a]



compd	R_1	R_2	X	H_1	H_2	H_3	Me	$SiMe_3$
1	Me	$SiMe_3$		3.40 (d)	4.02 (d)	5.17 (dd)	1.11 (s)	0.22 (s)
2	$SiMe_3$	Me		2.96 (dd)	3.73 (dd)	5.54 (dd)	1.35 (s)	0.26 (s)
3	Me	$SiMe_3$	PPh_3	3.02 (d)	3.05 (d)	5.55 (dd)	1.45 (d)	0.32 (s)
4	$SiMe_3$	Me	PPh_3	2.63 (dd)	2.84 (dd)	5.65 (dd)	1.85 (d)	0.20 (s)

[a] $CDCl_3$ solution, 60 MHz.

Table VI. Final Atomic Parameters of Non-Hydrogen Atoms for Complex 4

atom	x	y	z	B_{eq},[25] Å^2
Pd	0.143321 (19)	0.211461 (16)	0.22077 (3)	2.70
Cl	0.14640 (9)	0.20967 (7)	0.47650 (9)	4.03
P	−0.07532 (7)	0.23421 (6)	0.08939 (8)	2.30
Si	0.41427 (8)	0.32300 (7)	0.37689 (11)	3.11
C(1)	0.2032 (3)	0.2292 (3)	0.0344 (4)	3.65
C(2)	0.2941 (3)	0.1622 (3)	0.1340 (4)	3.46
C(3)	0.3569 (3)	0.1901 (3)	0.2902 (4)	3.00
C(4)	0.4263 (4)	0.1021 (3)	0.3921 (5)	4.56
C(5)	0.2879 (4)	0.4310 (3)	0.3339 (5)	4.58
C(6)	0.5393 (4)	0.3481 (3)	0.2987 (5)	4.40
C(7)	0.4873 (4)	0.3169 (4)	0.5909 (5)	5.01
C(11)	−0.1486 (3)	0.3599 (3)	0.1260 (4)	2.75
C(12)	−0.0906 (4)	0.4140 (3)	0.2687 (4)	4.14
C(13)	−0.1439 (5)	0.5090 (4)	0.3011 (5)	5.52
C(14)	−0.2514 (5)	0.5518 (3)	0.1964 (5)	5.13
C(15)	−0.3101 (4)	0.4994 (3)	0.0582 (5)	5.15
C(16)	−0.2585 (4)	0.4040 (3)	0.0216 (4)	3.93
C(21)	−0.1683 (3)	0.1406 (3)	0.1331 (4)	2.70
C(22)	−0.1031 (4)	0.0580 (3)	0.2190 (4)	3.47
C(23)	−0.1690 (4)	−0.0125 (3)	0.2584 (5)	4.41
C(24)	−0.2997 (5)	−0.0013 (3)	0.2136 (5)	4.95
C(25)	−0.3649 (4)	0.0790 (4)	0.1285 (5)	4.93
C(26)	−0.3005 (4)	0.1511 (3)	0.0873 (5)	3.88
C(31)	−0.1217 (3)	0.2206 (3)	−0.1205 (3)	2.64
C(32)	−0.1645 (3)	0.1271 (3)	−0.2042 (4)	3.28
C(33)	−0.1840 (4)	0.1142 (3)	−0.3600 (4)	4.01
C(34)	−0.1627 (4)	0.1930 (3)	−0.4344 (4)	4.25
C(35)	−0.1209 (4)	0.2855 (3)	−0.3536 (4)	4.39
C(36)	−0.1006 (4)	0.2994 (3)	−0.1975 (4)	3.61

(*E*)-Ethyl 5-(Trimethylsilyl)-2-carbethoxy-4-hexenoate (15). To a solution of **1** (135 mg, 0.5 mmol) and triphenylphosphine (577 mg, 2.2 mmol) in THF (2 mL) was added a solution of diethyl sodiomalonate prepared from 60% mineral oil dispersion of NaH (60 mg, 1.5 mmol) and diethyl malonate (332 mg, 2.0 mmol) in THF (2 mL), and the mixture was stirred for 24 h at ambient temperature. The solution was filtered, and the filtrate was concentrated, extracted with ether (15 mL), washed with water (15 mL × 2), and dried over anhydrous $MgSO_4$. The product was isolated in 60% yield by preparative TLC on silica gel (R_f 0.37–0.65, ethyl acetate/hexane = 1:9). (*E*)-Ethyl 5-(trimetylsilyl)-2-carbethoxy-4-hexenoate (**15**): IR (neat) 1735 (C=O), 1625 (C=C), 1250, 1037, 832, 742 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 9 H, $SiMe_3$), 1.27 (t, J = 7.0 Hz, 6 H, CH_2CH_3), 1.60–1.76 (m, 3 H, $=CCH_3$) 2.69 (t, J = 6.0 Hz, 2 H, CH_2), 3.39 (dd, J = 6.0, 8.0 Hz, 1 H, CH), 4.19 (q, J = 7.0 Hz, 4 H, CH_2CH_3), 5.62 (dt, J = 1.7, 5.1 Hz, 1 H, C=CH). Anal. Calcd for $C_{14}H_{26}O_4Si$: C, 58.70; H, 9.15. Found: C, 58.24; H, 9.10.

(*Z*)-Ethyl 5-(Trimethylsilyl)-2-carbethoxy-4-hexenoate (16). To a solution of the anti complex **2** (113 mg, 0.42 mmol) and triphenylphosphine (485 mg, 1.85 mmol) in THF (2 mL) was added a solution of diethyl sodiomalonate (1.26 mmol) (prepared by the same procedure as above) in THF (2 mL). After it had been stirring for 3 h at ambient temperature, the mixture was extracted with ether (15 mL), washed with water (15 mL × 2), and dried over anhydrous $MgSO_4$. Removal of ether left oily material containing yellow solids to which hexane was added to remove the solid material. The product of (*Z*)-vinylsilane **16** was isolated in 79% yield by preparative TLC on silica gel (R_f 0.42–0.56, ethyl acetate/hexane = 1:9). **16**: IR (neat) 1739 (C=O), 1622 (C=C), 1232, 1160, 1038, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 9 H, $SiMe_3$), 1.27 (t, J = 7.0 Hz, 6 H, CH_2CH_3), 1.70–1.79 (m, 3 $=CCH_3$), $=CCh_3$), 2.69 (t, J = 7.0 Hz, 2 H, CH_2), 3.32 (t, J = 7.0 Hz, 1 H, CH), 4.20 (q, J = 7.0 Hz, 4 H, CH_2CH_3), 5.85 (dt, J = 1.7, 5.6 Hz, 1 H, C=CH). Anal. Calcd for $C_{14}H_{26}O_4Si$: C, 58.70; H, 9.15. Found: C, 58.22; H, 9.09.

[(*E*)-1-Methyl-3-(methylphenylamino)-1-propenyl]trimethylsilane (17). To a solution of **1** (135 mg, 0.5 mmol) and triphenylphosphine (551 mg, 2.1 mmol) in THF (3 mL) was added a solution of *N*-methylaniline (268 mg, 2.5 mmol) in THF (2 mL), and the mixture was stirred for 24 h at room temperature. The filtered mixture was concentrated. Preparative TLC on silica gel (R_f 0.51, ethyl acetate/hexane = 1:9) gave [(*E*)-1-methyl-3-(methylphenylamino)-1-propenyl]trimethylsilane (**17**) in 83% yield. **17**: IR (neat) 1600 (C=C), 1250, 1212, 1200, 1107, 995, 947, 833, 742, 685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 9 H, $SiMe_3$), 1.69–1.83 (m, 3 H, $=CCH_3$), 2.88 (s, 3 H, NCH_3), 3.92 (d, J = 5.5 Hz, 2 H, CH_2), 5.53–5.83 (m, 1 H, =CH), 6.47–6.80 (m, 3 H, Ph), 6.97–7.32 (m, 2 H, Ph). Anal. Calcd for $C_{14}H_{23}NSi$: C, 72.03; H, 9.93; N, 6.00. Found: C, 71.81; H, 9.86; N, 5.82.

[(*Z*)-1-Methyl-3-(methylphenylamino)-1-propenyl]trimethylsilane (18). This compound was prepared by the reaction of **2** (0.135 mg, 0.5 mmol) and triphenylphosphine (551 mg, 2.1 mmol) and *N*-methylaniline (0.118 g, 1.1 mmol) in THF (5 mL). The product (46% yield) was purified by preparative TLC (SiO_2, ethyl acetate/hexane = 1:9). **18**: IR (neat) 1602 (C=C), 1350, 1248, 1102, 1034, 997, 835, 745, 687 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 9 H, $SiMe_3$), 1.68–1.83 (m, 3 H, $=CCH_3$), 2.88 (s, 3 H, NCH_3), 3.91 (d, J = 5.5 Hz, 2 H, CH_2), 5.75–6.00 (m, 1 H, =CH), 6.43–6.76 (m, 3 H, Ph), 6.97–7.30 (m, 2 H, Ph). Anal. Calcd for $C_{14}H_{23}NSi$: C, 72.03; H, 9.93; N, 6.00. Found: C, 72.17; H, 9.83; N, 6.04.

Procedure for Nuclear Overhauser Effects. The ^{1}H NMR spectra of complexes **1** and **2** (10 w/v% in $CDCl_3$) were taken at 27 °C on a JEOL FX-100 NMR spectrometer equipped with a JEOL-980B computer having 16K of data memory. The perturbed spectra (12 scans, repetition time 20 s) were recorded by irradiating the peak of Me or $SiMe_3$ group of the complexes. The normal spectra were taken by the off-resonance shifting (48–50 Hz) of the irradiation frequency as reference spectra. The difference NOE spectra were obtained by computation of the above two spectra.

X-ray Crystallographic Study of 4. Crystal data: $C_{25}H_{30}ClPPdSi$; M_r = 531.4; triclinic; space group $P\bar{1}$; a = 11.215 (3) Å = b = 13.012 (3) Å, c = 9.314 (2) Å, α = 95.50 (3)°, β = 111.51 (2)°, γ = 85.03 (2)°; U = 12.568 (5) Å^3; Z = 2, D_{calcd} = 1.404 g cm^{-3}; $F(000)$ = 544, μ(Mo$K\alpha$) = 9.50 cm^{-1}.

A well-shaped crystal and approximate dimensions of 0.30 × 0.35 × 0.45 mm was mounted on a Rigaku automated four-circle diffractometer. Intensity data were collected up to a 2θ value of 54.0° with Zr-filtered Mo$K\alpha$ radiation (λ = 0.71069 Å) at a room temperature (20 °C). The θ–2θ scan mode was employed at a 2θ rate of 4° min^{-1} with a scan width of $\Delta 2\theta = (1.8 + 0.70 \tan \theta)°$. Background intensities were measured for 5 s at both ends of a scan. Four standard reflections (700, 070, 0$\bar{7}$0, and 007) measured at regular intervals showed no intensity decrease throughout the data collection. A total of 5489 independent reflections was collected for the quadrants hkl, $\bar{h}kl$, $h\bar{k}l$, and $\bar{h}\bar{k}l$ ($h, k, l > 0$),

Table VII. Final Atomic Parameters of Hydrogen Atoms for Complex 4

atom	*x*	*y*	*z*	*B*, Å^2
H(1A)	0.203 (4)	0.306 (3)	0.049 (5)	2.3 (8)
H(1B)	0.158 (4)	0.204 (3)	−0.066 (5)	3.4 (10)
H(2)	0.293 (4)	0.095 (3)	0.099 (5)	2.4 (8)
H(4A)	0.399 (4)	0.030 (4)	0.333 (5)	4.0 (10)
H(4B)	0.514 (4)	0.101 (3)	0.423 (5)	3.3 (9)
H(4C)	0.404 (4)	0.108 (3)	0.482 (4)	2.0 (8)
H(5A)	0.239 (4)	0.422 (4)	0.374 (5)	3.6 (10)
H(5B)	0.248 (4)	0.440 (3)	0.235 (5)	3.2 (9)
H(5C)	0.323 (4)	0.492 (4)	0.381 (5)	3.8 (10)
H(6A)	0.603 (5)	0.299 (4)	0.320 (6)	4.4 (11)
H(6B)	0.505 (4)	0.340 (3)	0.184 (5)	3.2 (9)
H(6C)	0.567 (5)	0.408 (4)	0.333 (6)	5.4 (12)
H(7A)	0.429 (5)	0.290 (4)	0.636 (6)	5.0 (12)
H(7B)	0.556 (4)	0.272 (4)	0.621 (5)	3.7 (10)
H(7C)	0.503 (5)	0.382 (4)	0.649 (6)	4.6 (11)
H(12)	−0.013 (4)	0.382 (3)	0.343 (5)	2.8 (9)
H(13)	−0.102 (5)	0.547 (4)	0.396 (6)	5.2 (12)
H(14)	−0.288 (4)	0.616 (4)	0.216 (5)	3.8 (10)
H(15)	−0.385 (5)	0.520 (4)	−0.012 (6)	4.3 (11)
H(16)	−0.296 (4)	0.371 (3)	−0.071 (5)	2.4 (8)
H(22)	−0.013 (4)	0.052 (3)	0.250 (5)	2.2 (8)
H(23)	−0.127 (4)	−0.067 (3)	0.322 (5)	3.1 (9)
H(24)	−0.336 (4)	−0.052 (3)	0.247 (5)	3.0 (9)
H(25)	−0.448 (4)	0.086 (3)	0.088 (5)	3.3 (9)
H(26)	−0.342 (4)	0.199 (3)	0.029 (5)	2.4 (8)
H(32)	−0.176 (4)	0.073 (3)	−0.157 (5)	2.0 (8)
H(33)	−0.208 (4)	0.049 (3)	−0.414 (5)	3.1 (9)
H(34)	−0.174 (4)	0.183 (3)	−0.533 (5)	3.0 (9)
H(35)	−0.102 (4)	0.336 (3)	−0.404 (4)	1.9 (8)
H(36)	−0.074 (4)	0.358 (3)	−0.144 (5)	2.5 (8)

4906 of which were considered as observed ($|F_o| > 3\sigma(|F_o|)$) and used for the structure determination and refinement. The agreement factor between equivalent reflections ($R_{\mathrm{ref}} = \sum||F| - \langle|F|\rangle|/\sum|F|$) is 0.010, where $\langle|F|\rangle$ is the average value of equivalent reflections. Usual *Lp* corrections were applied but corrections for absorption and extinction effects were ignored.

The structure was solved by the conventional heavy-atom method and refined by the block-diagonal least-squares procedure (*HBLS*-V[23]), the function minimized being $\sum w(|F_o| - |F_c|)^2$. The anisotropic refinement for all the non-hydrogen atoms converged the *R* value ($R = \sum||F_o| - |F_c||/\sum|F_o|$) to 0.041. On the difference Fourier map calculated at this stage, all the hydrogen atoms were easily found, which were refined isotropically in the further refinement. At the final stage of refinement a strong reflection ($1\bar{2}1$) which was considered as highly affected by extinction was omitted. The final *R* and R_w indices are 0.031 and 0.040 for 4905 observed reflections, respectively, where $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$. The weighting scheme used is $w = (\sigma_{cs}{}^2 + a|F_o| + b|F_o|^2)^{-1}$, where σ_{cs} is the standard deviation estimated from the counting statistics and the parameters *a* and *b* used in the final cycle of refinement are 0.0012 and 0.0003, respectively. However, unit weights were employed only throughout the early stages of refinement. Atomic scattering factors were taken from ref 24 for non-hydrogen atoms and those of Stewart et al.[25] for hydrogen atoms. The final atomic parameters are presented in Tables VI and VII.

All the computations were carried out on an ACOS 850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Acknowledgment. We wish to thank Mr. Y. Terawaki for the nuclear Overhauser experiment.

Registry No. **1**, 98524-88-0; **2**, 98524-89-1; **3**, 98466-66-1; **4**, 98524-90-4; **5**, 98466-67-2; **6**, 98524-91-5; **15**, 98466-68-3; **16**, 98466-69-4; **17**, 98466-70-7; **18**, 98466-71-8; $PdCl_2$, 7647-10-1; trimethylvinylsilane, 754-05-2; diethyl malonate, 105-53-3; *N*-methylaniline, 100-61-8.

Supplementary Material Available: Tables of observed and calculated structure factors and anisotropic temperature factors and complete lists of bond distances and bond angles for **4** (22 pages). Ordering information is given on any masthead page.

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