Synthesis, Characterization, and Isomerization Behavior of *syn*-(μ-η^3-1-Methylallyl)(μ-benzenethiolato)bis(tricyclohexylphosphine)dipalladium(I), $((C_6H_{11})_3P)_2Pd_2$(*syn*-μ-η^3-$CH_2CHCHCH_3$)(μ-SC_6H_5), and Its Anti Isomer

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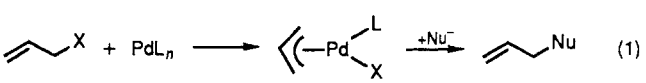
3-(Phenylthio)-1-butene reacts with $Pd(PCy_3)_2$ (PCy_3 = tricyclohexylphosphine) smoothly to give $(Cy_3P)_2Pd_2$(*anti*-μ-η^3-$CH_2CHCHCH_3$)(μ-SC_6H_5) (**1**). Reaction of 1-(phenylthio)-2-butene (*E*:*Z* = 78:22) with $Pd(PCy_3)_2$ gives a mixture of **1** and $(Cy_3P)_2Pd_2$(*syn*-μ-η^3-$CH_2CHCHCH_3$)(μ-SC_6H_5) (**2**) in a ratio of 31:69. The syn complex **2** is isomerized into its thermodynamically more stable anti isomer **1** obeying the first-order kinetics in the presence of olefins such as 4-phenyl-1-butene, 1-phenyl-2-butene, styrene, acrylonitrile, ethyl acrylate, ethyl methacrylate, and 3-(phenylthio)propene. Thermodynamic parameters for syn $\rightleftarrows$ anti equilibrium are $\Delta G° = -6.1$ kJ mol^{-1}, $\Delta H° = 5.6 \pm 0.2$ kJ mol^{-1}, and $\Delta S° = 36 \pm 2$ J mol^{-1} deg^{-1} at 323 K. The isomerization rates highly depend on the nature of added olefin in these reactions. The first-order rate constants of the isomerization promoted by 4-phenyl-1-butene vary in proportion to the concentration of the olefin.

Introduction

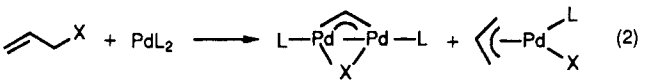
Oxidative addition of allylic compounds to Pd(0) compounds to give (η^3-allyl)palladium complexes combined with nucleophilic attack, as conceptually depicted in eq 1, has been extensively utilized in organic synthesis.[1] To



(1)

achieve high selectivity in these palladium-catalyzed reactions of allylic compounds, detailed information regarding the behavior of (η^3-allyl)palladium(II) complexes is required.

Recently it has been realized that not only the mononuclear (η^3-allyl)palladium(II) complexes but also dinuclear Pd(I) complexes with bridging η^3-allyl ligands[2-5] are involved in these reactions. For example, oxidative addition of allyl acetate or allyl phenyl sulfide to Pd(0) complexes give dinuclear Pd(I) compounds with a bridging η^3-allyl ligand in addition to mononuclear (η^3-allyl)palladium(II) complexes depending on the molar ratio of the reactants (eq 2). Furthermore, interconversion of the mononuclear



(2)

X = OAc, SPh; L = PCy_3, $P(t\text{-}Bu)_3$

complexes with dinuclear complexes on interaction with tertiary phosphine ligands or Pd(0) complexes has been established.[5]

Another complicating factor in these palladium-catalyzed allylation reactions is involvement of syn and anti η^3-allylic complexes regarding the configuration of the alkyl substituent attached to the η^3-allyl moiety. Relative stabilities of the syn and anti isomers of mononuclear Ni(II) and Pd(II) complexes and mechanisms of their mutual conversion have received considerable attention.[6-8] However, little studies have been made regarding the syn–anti isomerization of dinuclear palladium complexes mainly due to the lack of such isolated complexes having a bridging 1-alkyl-η^3-allyl ligand.

Recently we prepared dinuclear palladium(I) complexes having a bridging 1-alkyl-η^3-allyl ligand, $(Cy_3P)_2Pd_2$(μ-η^3-$CH_2CHCHCH_3$)(μ-SPh), by oxidative addition of 1-(phenylthio)-2-butene and 3-(phenylthio)-1-butene, respectively, with $Pd(PCy_3)_2$.[9] The former reaction gave a mixture of syn and anti complexes, while the latter mainly gave the anti complex. The syn complex undergoes isomerization to the anti form in the presence of olefin and/or PCy_3. In this paper we report the preparation and the characterization of the dinuclear syn and anti η^3-allylic

(1) For reviews: (a) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. (b) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: New York, 1980. (c) Trost, B. M.; Verhoeven, T. R. *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1982; Vol. 8, p 799. (d) Tsuji, J. *Pure. Appl. Chem.* **1982**, *54*, 197. (e) Trost, B. M. *J. Organomet. Chem.* **1986**, *300*, 263. (f) Tsuji, J. *J. Organomet. Chem.* **1986**, *300*, 281. (g) Tsuji, J. *Tetrahedron* **1986**, *42*, 4361. (h) Tsuji, J.; Minami, I. *Acc. Chem. Res.* **1987**, *20*, 140.

(2) Kobayashi, Y.; Iitaka, Y.; Yamazaki, H. *Acta Crystallogr.* **1972**, *B28*, 899.

(3) (a) Werner, H.; Tune, D.; Parker, G.; Krüger, C.; Brauer, D. J. *Angew. Chem.* **1975**, *87*, 205; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 185. (b) Werner, H. *Angew. Chem.* **1977**, *89*, 1; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 1. (c) Werner, H.; Kuhn, A. *Angew. Chem.* **1977**, *89*, 427; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 412. (d) Werner, H.; Kuhn, A.; Tune, D. J.; Krüger, C.; Brauer, D. J.; Sekutowski, J. C.; Tsay, Y.-H. *Chem. Ber.* **1977**, *110*, 1763. (e) Werner, H.; Kraus, H.-J. *Chem. Ber.* **1980**, *113*, 1072. (f) Werner, H. *Adv. Organomet. Chem.* **1981**, *19*, 155. (g) Werner, H.; Kraus, H.-J.; Thometzek, P. *Chem. Ber.* **1982**, *115*, 2914.

(4) Jolly, P. W.; Krüger, G.; Schick, K.-P.; Wilke, G. *Z. Naturforsch.* **1980**, *35B*, 926.

(5) (a) Yamamoto, T.; Saito, O.; Yamamoto, A. *J. Am. Chem. Soc.* **1981**, *103*, 5600. (b) Yamamoto, T.; Akimoto, M.; Yamamoto, A. *Chem. Lett.* **1983**, 1725. (c) Yamamoto, T.; Akimoto, M.; Saito, O.; Yamamoto, A. *Organometallics* **1986**, *5*, 1559.

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

(7) Tolman, C. *J. Am. Chem. Soc.* **1970**, *92*, 6777 and 6785.

(8) (a) Powell, J.; Shaw, B. L. *J. Chem. Soc. A* **1967**, 1839. (b) Powell, J. *Ibid.* **1971**, 2233. (c) Maitlis, P. M. *The Organic Chemistry of Palladium*; Academic Press: New York, 1971, pp 199, 210. (d) Vrieze, K. *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; p 441.

(9) Osakada, K.; Chiba, T.; Nakamura, Y.; Yamamoto, T.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1589.

0276-7333/89/2308-2602$01.50/0

Table I. NMR Data of Complexes 1 and 2

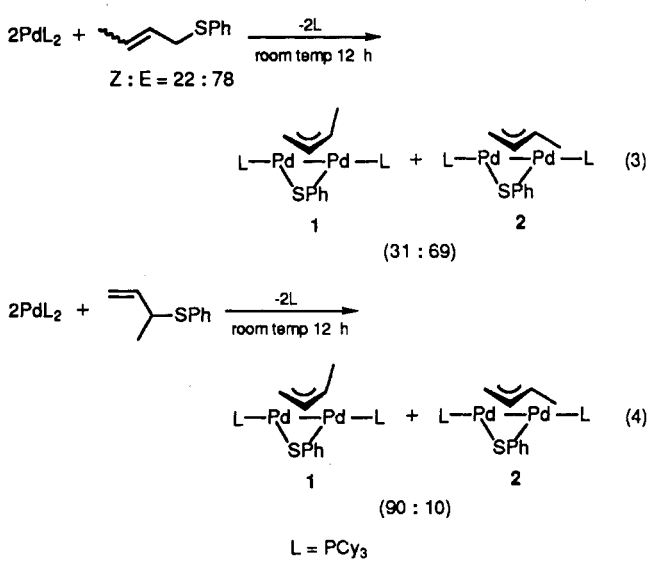
complex	^{1}H NMR,[a] ppm						^{13}C{^{1}H} NMR,[b] ppm				^{31}P{^{1}H} NMR,[c] ppm
	H^a	H^b	H^c	H^d	H^e	H^f	C^1	C^2	C^3	C^4	
1 (anti)	3.16	2.15	2.98	4.46		1.21	26.9	72.0	42.5	16.2	42.5, 47.1
$J(H^a\text{–}H^b)$ = 2 Hz, $J(H^a\text{–}H^c)$ = 8 Hz, $J(H^a\text{–}P)$ = 11 and 2 Hz, $J(H^b\text{–}H^c)$ = 13 Hz, $J(H^b\text{–}P)$ = 2 Hz, $J(H^c\text{–}H^d)$ = 8 Hz, $J(H^c\text{–}P)$ = 3 and 3 Hz, $J(H^d\text{–}H^f)$ = 6 Hz, $J(H^d\text{–}P)$ = 11 and 2 Hz, $J(H^f\text{–}P)$ = 6 Hz										$J(P\text{–}P)$ = 84 Hz
2[d] (syn)	3.33	1.71[e]	2.58		2.77	2.17[e]	30.5[e]	67.9	47.1	22.9	44.2, 48.6
$J(H^a\text{–}H^b)$ = 2 Hz, $J(H^a\text{–}H^c)$ = 8 Hz, $J(H^a\text{–}P)$ = 10 and 2 Hz, $J(H^b\text{–}H^c)$ = 12 Hz, $J(H^c\text{–}H^e)$ = 12 Hz, $J(H^c\text{–}P)$ = 4 Hz, $J(H^e\text{–}H^f)$ = 6 Hz, $J(H^e\text{–}P)$ = 3 Hz								$J(C^3\text{–}P)$ = 4 Hz			$J(P\text{–}P)$ = 70 Hz

[a] 500 MHz at room temperature in C_6D_6. [b] 125 MHz at room temperature in C_6D_6. [c] 40 MHz at room temperature in C_6D_6. Downfield from external PPh_3. [d] Not isolated. Spectra were recorded as a mixture of 1 and 2 (31:69). [e] Signals are overlapped with those of PCy_3 ligands. Chemical shifts of these signals are obtained from a ^{1}H–^{13}C{^{1}H} correlation spectrum, but values of $J(H^b\text{–}H^f)$ and $J(H^b\text{–}P)$ are not determined.

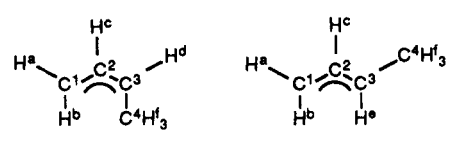
complexes as well as their mutual isomerization promoted by olefins.

Results and Discussion

Preparation and Characterization of Complexes $(Cy_3P)_2Pd_2(anti\text{-}\mu\text{-}\eta^3\text{-}CH_2CHCHCH_3)(\mu\text{-}SC_6H_5)$ (1) and $(Cy_3P)_2Pd_2(syn\text{-}\mu\text{-}\eta^3\text{-}CH_2CHCHCH_3)(\mu\text{-}SC_6H_5)$ (2). The reaction of 1-(phenylthio)-2-butene (*E*:*Z* = 78:22) with $Pd(PCy_3)_2$ proceeds smoothly at room temperature to give a mixture of 1 and 2 in a ratio of 31:69 in 12 h. Similar reaction of 3-(phenylthio)-1-butene with $Pd(PCy_3)_2$ predominantly gives 1 with a small amount of 2 in 24 h. Examination of the change in the ^{31}P{^{1}H} NMR spectrum of the reaction mixture in the latter reaction with time reveals the initial formation of an equimolar mixture of 1 and 2, the relative ratio of which changes gradually to 90:10. Recrystallization of the products gives 1 as yellow crystals. The NMR data (^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H}) of 1



and 2 are summarized in Table I. The designation of the carbon and hydrogen atoms in the η^3-allyl moieties in 1 and 2 is shown below. Although signals due to H^b and



H^f in the ^{1}H NMR spectrum of 2 and a signal due to C^1 in the ^{13}C{^{1}H} NMR spectrum of 2 are overlapped with those of PCy_3 ligands, the chemical shifts of these signals could be reasonably determined by means of ^{1}H–^{13}C{^{1}H} correlation spectroscopy. Assignment of the ^{13}C{^{1}H} NMR signals was confirmed by the off-resonance method. The ^{1}H NMR spectra of complexes with related structures, $L_2Pd_2(\mu\text{-}\eta^3\text{-}CH_2CRCH_2)(\mu\text{-}SC_6H_5)$ (R = H, CH_3; L = P(*i*-Pr)$_3$, PCy_3, and P(*t*-Bu)$_3$,[3g,5c] show signals due to syn, anti, and central hydrogens of the allyl ligands at 3.5–3.8, 1.6–1.9, and 2.5–2.8 ppm, respectively. Signals due to H^a, H^b, and H^c in the ^{1}H NMR spectra of 1 and 2 are assigned from similarity of the peak positions to those of the above known compounds as well as their splittings due to ^{1}H–^{1}H and ^{1}H–^{31}P couplings. Signals due to H^d in 1 and H^e in 2 appear at a magnetic field 1 ppm lower than those of the syn and anti hydrogens of the bridging unsubstituted allyl ligands of the already reported palladium μ-thiolato complexes.[3g,5c]

Syn and anti hydrogens in the ^{1}H NMR spectra of the allylic ligands couple with the central hydrogen, with coupling constants of approximately 7–8 and 11–13 Hz, respectively, both in mononuclear η^3-allylic palladium(II) complexes,[8b,10] and in the dinuclear μ-η^3-allylic palladium(I) complexes.[3g,5c] Also in complexes 1 and 2, coupling constants of H^c with H^a and H^b are 8 and 12 (or 13) Hz, respectively. Values of $J(H^c\text{–}H^d)$ in 1 (8 Hz) and $J(H^c\text{–}H^e)$ in 2 (12 Hz) indicate structures with the methyl group at the anti position for 1 and the syn position for 2. This assignment of the structures for 1 and 2 agrees with the observation that the reaction of *E*-rich 1-(phenylthio)-2-butene (*E*:*Z* = 78:22) with $Pd(PCy_3)_2$ gives the syn complex 2 as a major product (2:1 = 69:31) with retention of the configuration of the substrate although 2 is the thermodynamically less stable isomer (vide infra).

Isomerization of 2 to 1 Promoted by Olefins. The ^{31}P{^{1}H} NMR spectra of a mixture of 1 and 2 (31:69) obtained by reaction 3 show that the ratio of the isomers does not change when the mixture was left standing at room temperature in benzene. Raising the temperature to 60 °C does not vary the isomer ratio either. However, addition of 4-phenyl-1-butene at room temperature causes a relative increase in the amount of 1 at the expense of 2 to give a mixture rich in 1, indicating that the isomerization of 2 to 1 occurs in the presence of the olefin. Styrene also promotes similar isomerization, although the reaction is much slower than the isomerization promoted by 4-phenyl-1-butene. The isomerization of a mixture of 1 and 2 ([1] + [2] = 0.10 M) is completed in 30 min at 35 °C in the presence of 3.0 M 4-phenyl-1-butene to give a mixture of 1 and 2 in a ratio of 89:11. The similar reaction starting from 1 also gives a mixture of 1 and 2 in the same ratio,

(10) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA 1987; p 175.

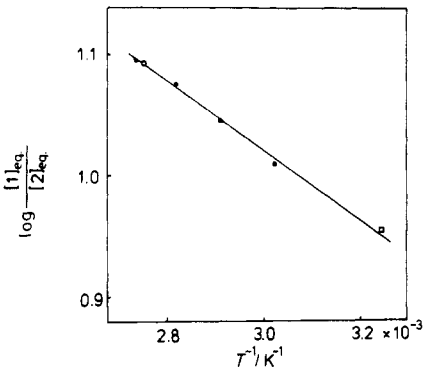


Figure 1. Temperature dependence of equilibrium constants for $K = [1]_{eq}/[2]_{eq}$: ●, (1 + 2 (31:69)) + styrene; ○, 1 + styrene; □, (1 + 2 (31:69)) + 4-phenyl-1-butene.

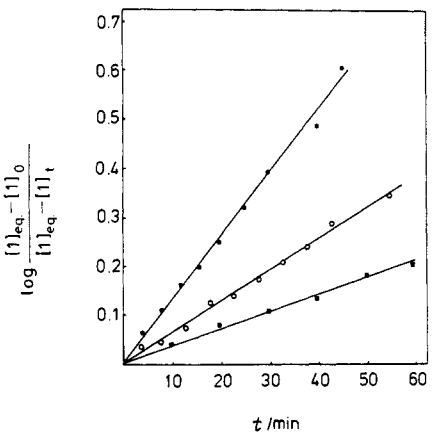


Figure 2. First-order plots of the isomerization of 2 to 1 promoted by 4-phenyl-1-butene. [1 + 2] = 50–60 mM. [CH_2=$CHCH_2CH_2Ph$] = 0.24 M (■), 0.42 M (○), and 0.75 M (●).

indicating the attainment of an equilibration. Thermodynamic parameters for the equilibrium 2 ⇄ 1 have been obtained as $\Delta G° = -6.1$ kJ mol^{-1}, $\Delta H° = 5.6 \pm 0.2$ kJ mol^{-1}, and $\Delta S° = 36 \pm 2$ J mol^{-1} deg^{-1} at 323 K from the temperature dependence of the equilibrium constants (Figure 1). The reason for the production of a mixture of 1 and 2 at room temperature (ca. 25 °C) in a ratio of 90:10 in the reaction of $Pd(PCy_3)_2$ and 3-(phenylthio)-1-butene after 24 h may be ascribed to the effect of 3-(phenylthio)-1-butene similar to that of 4-phenyl-1-butene to promote the equilibration of 1 and 2.

Relative stability of the anti isomer 1 to its syn isomer 2 is different from the trend in mononuclear (1-alkyl-η^3-allyl)palladium(II) complexes[11] in which the syn form is generally much more stable than the anti isomer. The relative stability of 2 to 1 may be due to steric repulsion between the methyl group located at the syn position of the μ-η^3-allyl ligand and the cyclohexyl group of the ligating PCy_3, the cone angle of which is quite large.[12] In the mononuclear palladium(II) η^3-allylic complexes also, relative stability of syn to anti isomer sometimes varies depending on the steric features of the complexes. For example, bulky substituents such as *t*-Bu and $SiMe_3$ groups on the η^3-allylic ligand tend to prefer an anti position due to the steric repulsion between the bulky substituent at the syn position of the allylic ligand and the other ligand in the coordination plane of the square-planar structure.[6b,13]

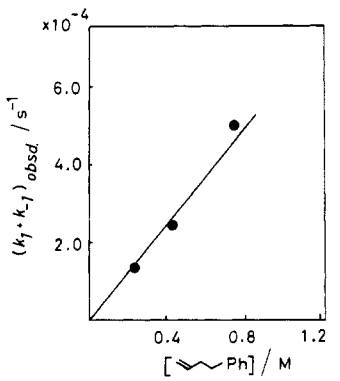


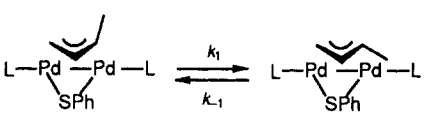
Figure 3. Dependence of observed rate constants of the isomerization on concentration of 4-phenyl-1-butene.

Table II. Isomerization of 2 to 1 Promoted by Olefins[a]

olefin	concn, M	temp, °C	$k_1 + k_{-1}$, s^{-1}	$(k_1 + k_{-1})$/[olefin], s^{-1} M^{-1}
CN	0.30	41	6×10^{-3}	2×10^{-2}
COOEt	0.33	41	4×10^{-3}	1×10^{-2}
SPh	0.21	41	5.3×10^{-4}	2.5×10^{-3}
Ph	0.24	41	1.4×10^{-4}	
	0.42	41	2.5×10^{-4}	6.2×10^{-4}[b]
	0.75	41	5.1×10^{-4}	
Ph	0.35	41	2.0×10^{-5}	5.8×10^{-5}
COOEt	0.33	41	1.7×10^{-5}	5.2×10^{-5}
Ph	0.97	54	1.2×10^{-4}	1.2×10^{-4}

[a] Reaction was carried out in benzene containing 20% benzene-d_6 at complex concentrations of 50–60 mM. [b] Averaged value of the observed rate constants at three olefin concentrations.

The isomerization of 2 to 1 promoted by 4-phenyl-1-butene obeys the first-order kinetics as revealed by $^{31}P\{^1H\}$ NMR spectroscopy. Signals due to the other complex than 1 and 2 are not observed in the course of the reaction.



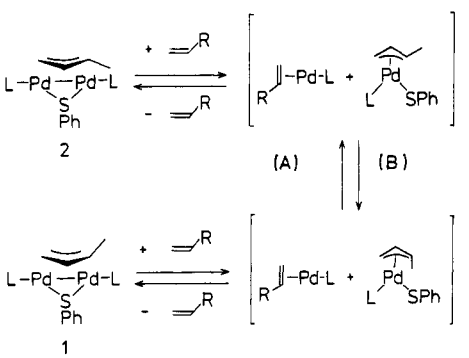
1 2 (5)

Figure 2 shows the first-order plots obtained at several concentrations of the olefin. The observed rate constants k_1 and k_{-1} vary in proportion to the concentration of the added olefin (Figure 3). Other olefins such as 1-phenyl-2-butene, ethyl acrylate, ethyl methacrylate, and acrylonitrile also cause similar isomerization of 2 to 1. Compounds without an olefinic C=C double bond such as ethyl propionate, diphenyl sulfide, and 1-(phenylthio)propane do not promote the isomerization at all.

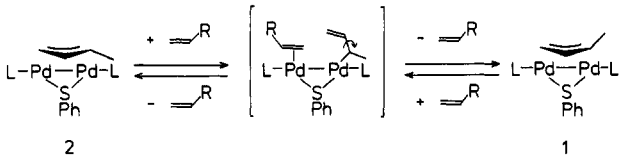
Table II summarizes the observed rate constants of the isomerization promoted by these olefins. The nature of the added olefins influences the rate of the reaction. Isomerization in the presence of disubstituted olefins such as ethyl methacrylate and 1-phenyl-2-butene is much slower than the reaction promoted by the corresponding monosubstituted olefins such as ethyl acrylate and 4-phenyl-1-butene, respectively. Among the monosubstituted olefins the compounds having electron-withdrawing

(11) Wilkinson, G., Stone, F. G. A., Abel, F., Eds. *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1982; Vol. 6.
(12) Tolman, C. A. *Chem. Rev.* **1975**, *77*, 313.
(13) Ohta, T.; Hosokawa, T.; Murahashi, S.; Miki, K.; Kasai, N. *Organometallics* **1985**, *4*, 2080.

Scheme I



Scheme II



groups such as ethyl acrylate and acrylonitrile show larger effects than olefins having a less electron-withdrawing substituent in promoting the reaction.

Several processes causing the isomerization of the syn isomer **2** to its anti isomer **1** are conceivable. (i) The interaction of olefin with **2** may initiate the reductive elimination of the allylic sulfide from **2** and its reoxidative addition. A syn–anti isomerization may occur during the reductive elimination and oxidative addition processes. (ii) The olefin may cause breaking up of the dinuclear palladium complex to a mixture of an olefin-coordinated Pd(0) species (A) and a mononuclear η^3-allylic Pd(II) complex (B) as shown in Scheme I. The mononuclear η^3-allylic complex thus formed may undergo syn–anti isomerization to give its isomeric η^3-allylic complex that combines with the olefin-coordinated Pd(0) complex to generate the isomerized μ-η^3-allylic dinuclear palladium complex. (iii) The olefin may coordinate to one of the palladium atoms in the μ-allylic complex to give a PhS-bridged complex in which the two palladium atoms bind the olefin and η^1-allylic ligand, respectively, as shown in Scheme II. The subsequent rotation of the vinyl group in the η^1-allylic ligand followed by an η^1–η^3 conversion with liberation of the coordinated olefin may give the thermodynamically more stable form of the dinuclear μ-η^3-allylic complex.

At present we do not have sufficient experimental data to compare probability among these pathways for the syn–anti isomerization promoted by the olefins other than 3-(phenylthio)propene. The reversible reductive elimination–oxidative addition processes may be involved in the system because addition of 3-(phenylthio)propene to the reaction system containing **1** and **2** produced a small amount (7%) of $(Cy_3P)_2Pd_2(\mu\text{-}\eta^3\text{-}C_3H_5)(\mu\text{-}SC_6H_5)$ having a bridging unsubstituted allyl ligand. However, the syn–anti isomerization process seems to proceed much faster than formation of $(Cy_3P)_2Pd_2(\mu\text{-}\eta^3\text{-}C_3H_5)(\mu\text{-}SC_6H_5)$ since the yield of the unsubstituted allyl complex in the reaction mixture is so small even after completion of the syn–anti isomerization.[14] The above results suggest that mechanism i is less plausible than the others. We cannot decide whether mechanism ii or mechanism iii is operative for the above isomerization at present.[15]

In summary this work presents the first example of the preparation of dinuclear palladium(I) complexes with a bridging 1-alkyl-η^3-allyl ligand as well as their syn–anti isomerization promoted by the addition of an olefin.

Experimental Section

All manipulations of the complexes were carried out under nitrogen or argon atmosphere. $Pd(PCy_3)_2$,[16] 1-(phenylthio)-2-butene, 3-(phenylthio)-1-butene, and 3-(phenylthio)propene[17] were prepared according to the literature. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL JNM-FX-100 or a GX-500 spectrometer.

Reaction of 3-(Phenylthio)-1-butene with $Pd(PCy_3)_2$. To a benzene (5-mL) solution of $Pd(PCy_3)_2$ (0.51 g, 0.77 mmol) was added 3-(phenylthio)-1-butene (0.12 g, 0.76 mmol) at room temperature. The reaction mixture immediately turned to a yellow solution. $^{31}P\{^1H\}$ NMR analysis of the reaction mixture showed the presence of **1** with a small amount of **2** after being stirred for 24 h. Then the solvent was removed under reduced pressure. Addition of acetone (5 mL) to the resulting oily material caused the formation of a pale yellow solid, which was separated by filtration and recrystallized from hexane (10 mL) to give yellow crystals of complex **1** (0.27 g, 75%), mp 193–195 °C dec. Anal. Calcd for $C_{46}H_{78}P_2SPd_2$: C, 58.9; H, 8.4; S, 3.4. Found: C, 58.4; H, 8.6; S, 3.2.

Reaction of 1-(Phenylthio)-2-butene with $Pd(PCy_3)_2$. To a benzene (10-mL) solution of $Pd(PCy_3)_2$ (1.2 g, 1.8 mmol) was added a mixture of (*E*)- and (*Z*)-1-(phenylthio)-2-butene (*E*:*Z* = 78:22) (0.88 g, 5.4 mmol) at room temperature. The solution became dark yellow and then gradually turned pale yellow. After the solution was stirred for 12 h, the solvent was removed under reduced pressure. Addition of acetone (10 mL) followed by agitation of the reaction mixture caused the formation of a pale yellow solid, which was recrystallized from hexane (10 mL) to give a mixture of **1** and **2** (0.66 g, 78%). The ratio of **1** to **2** was determined as 31:69 from the ^1H NMR spectrum. Isolation of **2** by repeated recrystallization was unsuccessful.

$^{31}P\{^1H\}$ NMR analysis of the reaction mixture revealed the following course of the reaction. After the mixture was stirred for 7 h at room temperature, $Pd(PCy_3)_2$ was consumed completely and the ratio turned to 60:40 after being stirred for 24 h.

Equilibrium Measurement. An NMR sample tube containing a toluene solution of **1** (30 mM) and styrene (0.8 M) was heated at 90 °C in a thermostated bath for 24 h. The ratio of **1** to **2** was obtained from $^{31}P\{^1H\}$ NMR spectrum measured at 90.2 °C. The peak area ratio of $^{31}P\{^1H\}$ NMR spectra of **1** and **2** was calibrated by measurement of ^1H and $^{31}P\{^1H\}$ NMR spectra of three samples containing **1** and **2** in several ratios at room temperature. The relationship thus obtained of peak area ratios between ^1H and $^{31}P\{^1H\}$ NMR spectra was used to estimate the relative ratio of **1** and **2** from $^{31}P\{^1H\}$ NMR spectra.

Equilibrium constants under other conditions were obtained analogously.

Registry No. **1**, 108638-50-2; **2**, 108691-90-3; $Pd(PCy_3)_2$, 33309-88-5; 3-(phenylthio)-1-butene, 701-75-7; (*E*)-1-(phenylthio)-2-butene, 36195-56-9; (*Z*)-1-(phenylthio)-2-butene, 36195-55-8; acrylonitrile, 107-13-1; ethyl acrylate, 140-88-5; 3-(phenylthio)propene, 5296-64-0; 4-phenyl-1-butene, 768-56-9; 1-phenyl-2-butene, 1560-06-1; ethyl methacrylate, 97-63-2; styrene, 100-42-5.

(14) Reaction of $Pd(PCy_3)_2$ with an equimolar mixture of 3-(phenylthio)propene and 3-(phenylthio)-1-butene at room temperature gave $(Cy_3P)_2Pd_2(\mu\text{-}\eta^3\text{-}C_3H_5)(\mu\text{-}SC_6H_5)$ as a main product (>90% by NMR) in a few minutes, indicating that oxidative addition of 3-(phenylthio)-propene to the Pd(0) complex is much faster than that of 3-(phenylthio)-1-butene. Oxidative addition of 4-(phenylthio)-2-butene to $Pd(PCy_3)_2$ is still slower than that of 3-(phenylthio)-1-butene. See ref 9.

(15) As an attempt to shed light on the reaction mechanism we carried out a crossover experiment by NMR measurement of mixtures of $(i\text{-}Pr_3P)_2Pd_2(\mu\text{-}CH_2CMeCH_2)(\mu\text{-}SPh)$ and complexes **1** and **2** in the presence of olefins (acrylonitrile and 3-(phenylthio)-1-propene). $^{31}P\{^1H\}$ NMR spectra of the mixtures show formation of a multitude of complexes assignable to dinuclear complexes containing both PCy_3 and $P(i\text{-}Pr)_3$ ligands. However, the obtained spectra are similar to the spectrum of a mixture without added olefins, indicating that this exchange of the phosphine ligand is not influenced by olefins and is independent of the syn–anti isomerization processes.

(16) Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. *J. Am. Chem. Soc.* **1976**, *98*, 5850.

(17) Hurd, C. D.; Greengard, H. *J. Am. Chem. Soc.* **1930**, *52*, 3357.