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Substitution of Cl Atom in (2-Chloromethylallyl)palladium Complexes with Soft and Hard Nucleophiles

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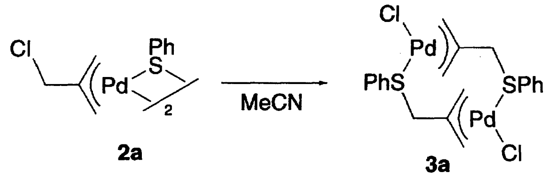
$[Pd\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}(\mu\text{-}SPh)]_2$ is spontaneously transformed, in MeCN, into $[Pd\{\eta^3\text{-}CH_2C(CH_2SPh)CH_2\}(Cl)]_2$, which has a novel thioether-bridged dimeric structure. This transformation is suggested to proceed by an attack of the thiolate anion at the methylene carbon bearing a Cl substituent of an ionic intermediate, $[Pd\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}(MeCN)_2]^+$. $[Pd\{\eta^3\text{-}CH_2C(CR_2Cl)CH_2\}(\mu\text{-}SPh)]_2$ (R = H, Me) reacts with PPh_3 to give $[Pd\{\eta^3\text{-}CH_2C(CH_2SPh)CR_2\}(Cl)(PPh_3)]$. This transformation proceeds via an attack of the thiolate anion at the terminal allyl carbon of an ionic intermediate, $[Pd\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}(PPh_3)_2]^+$, to give 2-phenylthiomethylallyl chloride, which undergoes an oxidative addition to the resulting Pd(0) complexes. $[Pd\{\eta^3\text{-}CH_2C(CR_2Cl)CH_2\}(Cl)(PPh_3)]$ (R = H, Me) reacts with $Bu_3SnCH{=}CH_2$ to give $[Pd\{\eta^3\text{-}CH_2C(CH_2CH{=}CH_2)CR_2\}(Cl)(PPh_3)]$ through a reductive elimination–oxidative addition sequence, starting from an intermediate, $[Pd\{\eta^3\text{-}CH_2C(CR_2Cl)CH_2\}(CH{=}CH_2)(PPh_3)]$.

The transformations of (η^3-allyl)palladium complexes, by which a new substituent is introduced into the allyl moiety, are interesting from the standpoint of organic synthesis, because of the versatile reactivities of allylic palladium complexes, such as nucleophilic substitution reactions.[1] Recent examples include a nucleophilic attack at an allylic central carbon bearing a leaving group (e.g. Cl or OR) to give multi-substituted allylic compounds[2a] or 2-substituted (η^3-allyl)palladium complexes.[2b] We have recently reported on the formation of $[Pd\{\eta^3\text{-}CH_2C(CH_2C_5H_5)CH_2\}(\mu\text{-}Cl)]_2$ from $[Pd\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}(\eta^5\text{-}C_5H_5)]$ in which a trimethylenemethane (TMM)-palladium intermediate undergoes an intermolecular electrophilic substitution with a cyclopentadienyl ligand (Scheme 1).[3] Here, we report on different types of substitution reactions and their mechanisms by which the Cl atom of (η^3-2-chloromethylallyl)palladium complexes is replaced by nucleophiles, such as thiolate and vinyl groups; these groups attack either at the Cl–CH_2 carbon or the allyl terminal carbon, the latter step being followed by the oxidative addition of Pd(0) and the allylic chloride generated by this step.

Results and Discussion

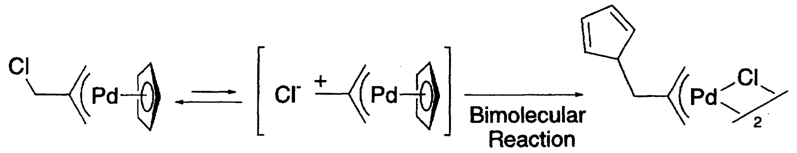
Reaction of $[Pd\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}(\mu\text{-}SPh)]_2$ with MeCN. A treatment of $[Pd\{\eta^3\text{-}CH_2C(CR_2Cl)CH_2\}Cl]_2$ (**1a**: R = H, **1b**: R = Me) with TlSPh gives $[Pd\{\eta^3\text{-}CH_2C(CR_2Cl)CH_2\}(\mu\text{-}SPh)]_2$ (**2a**: R = H, **2b**: R = Me). Complex **2a** was stable in C_6D_6 and $CDCl_3$ for several days, but reacted with MeCN at room temperature for 3 d, leading to the isolation of a pale-yellow precipitate of $[Pd\{\eta^3\text{-}CH_2C(CH_2SPh)CH_2\}Cl]_2$ (**3a**) in 64% isolated yield (Eq. 1).



(1)

The ${}^1H$ NMR spectrum of **3a** exhibited two methylene protons (δ = 3.59, 5.06) and two *syn* and two *anti* protons (δ = 3.19, 3.55, 4.53, 4.93), indicating an asymmetric structure; the molecular weight by the vapor-pressure osmometry method in $CHCl_3$ was found to be 665, which was close to that expected from a dimer of **3a** (610). In addition, the structure was confirmed by X ray diffraction (Fig. 1). Thus, the complex dimerizes not through a more conventional Cl-bridge, but through an unusual CH_2S bridge.

As for the reaction mechanism, we first assumed an attack of the thiolate anion on the terminal allyl carbon of an ionic intermediate, $[Pd\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}(MeCN)_2]^+$ (**A**), to give 2-phenylthiomethylallyl chloride (**B**) (Path a in Scheme 2), followed by its oxidative addition to the resulting Pd(0) to afford **3a**. However, this does not agree with the absence of an oxidative addition product, $[Pd\{\eta^3\text{-}$



Scheme 1.

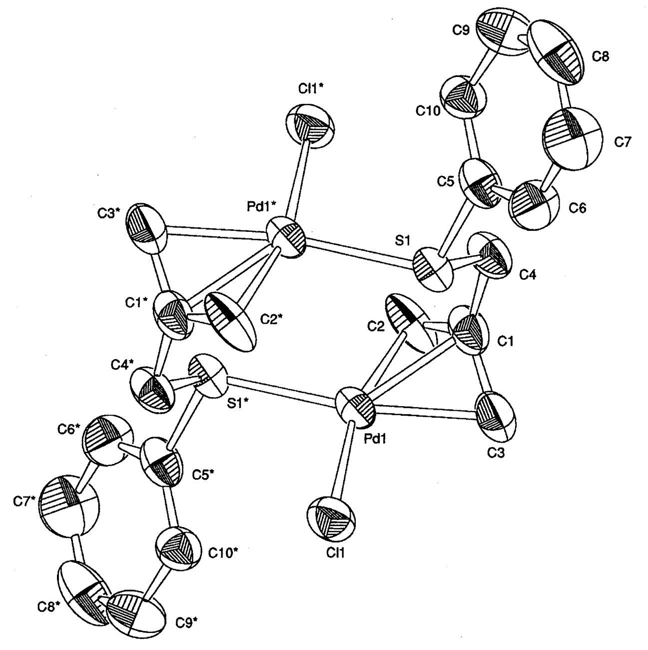
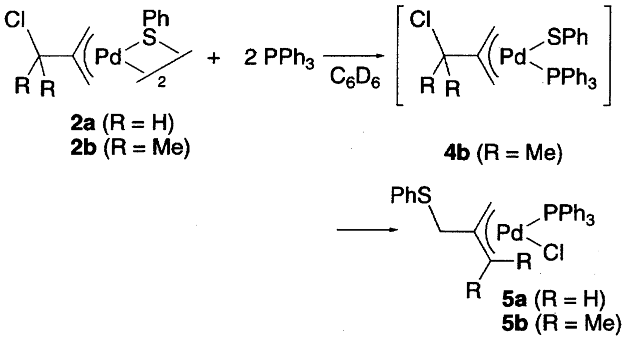


Fig. 1. ORTEP drawing of complex **3a** with thermal ellipsoids at 50% probability levels. All hydrogen atoms and 2 mols of $CHCl_3$ in the lattice are omitted for clarity.

$CH_2CHCH_2\}(Cl)]_2$, in the reaction of **2a** in the presence of excess allyl chloride (10 molar amounts) in MeCN for 3 d. Furthermore, $[Pd\{\eta^3\text{-}CH_2CHCH_2\}(\mu\text{-}SPh)]_2$ (**2c**) gave no C–S coupling product under the same conditions as that for Eq. 1, suggesting that only the chloromethyl group at the 2 position induces the transformation shown in Eq. 1. Of further significance is that the Me substituted derivative, $[Pd\{\eta^3\text{-}CH_2C(CMe_2Cl)CH_2\}(SPh)]_2$ **2b**, showed no reactivity in MeCN for several days.

On the basis of the experimental results described above, thiolate is expected to attack at the methylene carbon bearing Cl of **A** to give complex **C** (Path b in Scheme 2), which further dimerizes to give thermodynamically preferred **3a**. This is consistent with the fact that **2b** did not undergo the above-mentioned dimerization, because the steric hindrance by two Me groups of **A** prevents a thiolate attack. Although (π-allyl)palladium thiolates, such as **2**, may give an ionic intermediate **A** in MeCN transiently, free thiolate would not attack the terminal allyl carbon of **A**, because such an attack would lead to the formation of the Pd(0) species, but MeCN lacks the ability to stabilize the Pd(0) state sufficiently.[4)]

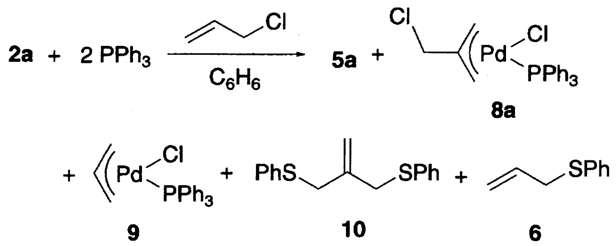
Reaction of 2a, b with PPh_3. The addition of PPh_3 ($Pd/PPh_3=1$) to **2a** in C_6D_6 at 25 °C gave **5a** in 80% yield after 7 h (Eq. 2). No intermediate was observed throughout the reaction. On the contrary, the reaction of **2b** with PPh_3 in C_6D_6 at 25 °C afforded $[Pd\{\eta^3\text{-}CH_2C(CMe_2Cl)CH_2\}(SPh)\text{-}(PPh_3)]$ (**4b**) in 98% NMR yield for 10 min. The structure of **4b** was assigned based on its ^1H NMR spectrum, which exhibits two singlet at $\delta=1.37$ and 1.42, corresponding to two diastereotopic Me groups and four inequivalent signals at $\delta=2.43$, 3.11, 3.34, and 3.35 corresponding to terminal π-allyl protons. Complex **4b** was transformed into **5b** completely in 4 h (Eq. 2).



(2)

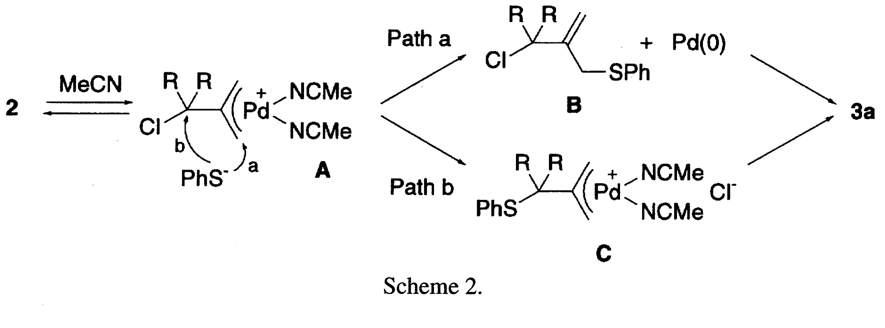
These reactions provide different products from that of our previous reaction of $[Pd\{\eta^3\text{-}CH_2CHCH_2\}(\mu\text{-}SPh)]_2$ **2c** with PPh_3 to give $[Pd_2(\mu\text{-}C_3H_5)(\mu\text{-}SPh)(PPh_3)_2]$ (**7**), probably through the coupling of **2c** with $Pd(PPh_3)_2$, resulting from a reductive elimination of allyl(phenyl)sulphide (**6**) from **2c** (Scheme 3).[5)]

The addition of PPh_3 to **2a** in the presence of excess allyl chloride (5 mol. amounts) gave a mixture of **5a** (68%), $[Pd\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}(Cl)(PPh_3)]$ (**8a**) (13%) and $[Pd\{\eta^3\text{-}CH_2CHCH_2\}(Cl)(PPh_3)]$ (**9**) (15%) together with phenyl 2-(phenylthiomethyl)allyl sulfide (**10**) (16%) and **6** (3%) (Eq. 3).

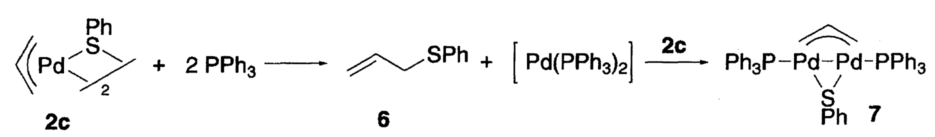


(3)

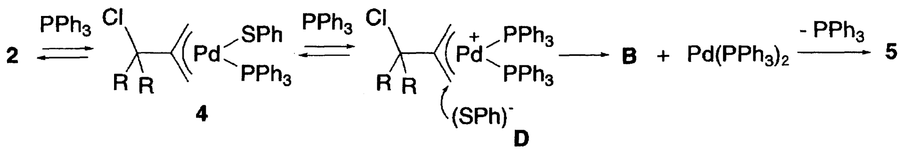
A proposed mechanism for Eq. 2 is shown in Scheme 4. By the reaction of **2** with PPh_3 ($Pd/PPh_3=1.0$), the thiolate



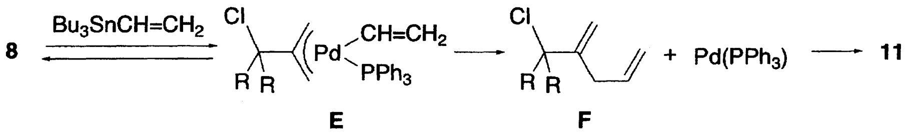
Scheme 2.



Scheme 3.



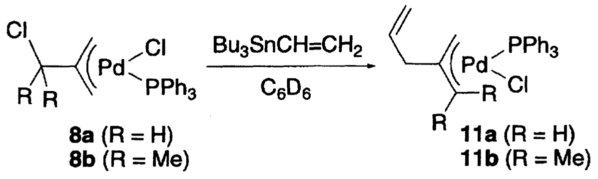
Scheme 4.



Scheme 5.

bridge in **2** is split to form **4**. Although **4a** was not detected, **4b** was unambiguously confirmed to exist transiently. The transient complex **4** may be transformed into the ionic intermediate **D** when attacked by even a small amount of another PPh_3, which exists due to incompleteness of the first PPh_3 coordination to **2**. Intermediate **D** would then give **B** and Pd(0), both of which would rapidly undergo an oxidative addition to give **5**. The formation of **9** in the reaction carried out in the presence of allyl chloride (Eq. 3) clearly proves the generation of a Pd(0) species. Notice that the thiolate acts as a soft nucleophile which approaches the terminal allyl carbon of **D** by an external attack process.[5] The thiolate anion of **4a** is also expected to attack at added allyl chloride[6] or **B** to give **6** or **10** together with **8a**.

Reaction of 2 with $Bu_3SnCH{=}CH_2$. $[Pd\{\eta^3\text{-}CH_2C(CR_2Cl)CH_2\}(Cl)(PPh_3)]$ (**8a**: R=H, **8b**: R=Me) were readily synthesized by the treatment of **1a** and **1b** with PPh_3. The addition of an equimolar amount of $Bu_3SnCH{=}CH_2$ to **8a** and **8b** in C_6D_6 at 25 °C gave $[Pd\{\eta^3\text{-}CH_2C(CH_2CH{=}CH_2)CR_2\}(Cl)(PPh_3)]$ (**11a**: R=H, **11b**: R=Me) in 92 and 86% NMR yields, respectively, in 4 h. The same reaction in the presence of excess allyl chloride (5 molar amounts) gave a mixture of **8a** (22%), **9** (35%), and **11a** (41%) for 4 h, suggesting the formation of Pd(0) as an intermediate.



(4)

Judging from the fact that the reaction of **8a** with $Bu_3SnCH{=}CH_2$ gave Pd(0) as an intermediate and the vinyl group acts as a hard nucleophile which attacks at the terminal allyl carbon through the initial Pd–vinyl bond formation and subsequent reductive elimination,[7] the mechanism for Eq. 4 is proposed in Scheme 5. Transmetallation between **8** and $Bu_3SnCH{=}CH_2$ would afford an intermediate **E**. This may undergo reductive elimination to give Pd(0) and **F**, which is followed by oxidative addition to eventually give **11**.

In summary, we have presented three routes to η^3-2-phenylthiomethylallyl and 2-(allyl)allyl complexes of palladium from (η^3-2-chloromethylallyl)palladium complexes. Although they look superficially like similar transformations to each other, their precise reaction courses are different.

Experimental

General Procedure. All of the manipulations were carried out under argon using standard vacuum-line techniques. The solvents were dried by standard methods and distilled prior to use. (η^3-Allyl)palladium complexes **1a**[8] and **1b**[9] were prepared according to the reported methods. The reagents were of commercial grade and used without purification. The ^{1}H NMR spectra were recorded on a JEOL JNM-GSX-270 (270 MHz) spectrometer. Chemical shifts in the ^{1}H NMR were referenced to residual protons of the solvent. The molecular weight (MW) was measured on a Corona 114 molecular-weight apparatus at 40 °C.

Synthesis of $[Pd\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}(\mu\text{-}SPh)]_2$ (2a). To a suspension of **1a** (1.00 g, 4.32 mmol) in C_6H_6 (10 mL) was added TlSPh (1.20 g, 4.54 mmol) at room temperature, the mixture was stirred for 6 h. TlCl was removed by filtration; a yellow solution was concentrated. Recrystallization from C_6H_6/hexane yielded crystals of **2a** (1.00 g). Yield: 76%. ^{1}H NMR (C_6D_6) $\delta = 7.76$ (d, $J = 6.8$ Hz, 2H), 6.99 (m, 3H), 3.34 (s, 2H), 3.26 (s, 2H), 2.54 (s, 2H). Found: C, 39.60; H, 3.80%. Calcd for $C_{10}H_{11}ClPdS$: C, 39.36; H, 3.63%.

Synthesis of $[Pd\{\eta^3\text{-}CH_2C(CMe_2Cl)CH_2\}(\mu\text{-}SPh)]_2$ (2b). This was prepared from **1b** in a similar manner to that for **2a**. Yield: 62%. ^{1}H NMR (C_6D_6) $\delta = 7.82$ (d, $J = 7.2$ Hz, 2H), 6.9—7.1 (m, 3H), 3.65 (br s, 2H), 2.54 (br s, 2H), 1.45 (s, 6H). Found: C, 43.44; H, 4.42%. Calcd for $C_{12}H_{15}ClPdS$: C, 43.26; H, 4.54%.

Synthesis of $[Pd\{\eta^3\text{-}CH_2C(CH_2SPh)CH_2\}(Cl)]_2$ (3a). An MeCN (10 mL) solution of **2a** (405 mg, 1.03 mmol) was stirred for 72 h. The resulting pale-yellow precipitate of **3a** was collected by a suction filter, washed with pentane and dried in a vacuum (261 mg). Yield: 64%. ^{1}H NMR ($CDCl_3$) $\delta = 8.04$ (m, 2H), 7.42 (m, 3H), 5.07 (d, $J = 10.3$ Hz, 1H), 4.93 (d, $J = 3.0$ Hz, 1H), 4.53 (br s, 1H), 3.59 (d, $J = 10.3$ Hz, 1H), 3.56 (d, $J = 3.0$ Hz, 1H), 3.19 (br s, 1H). Found: C, 39.07; H, 3.67%. Calcd for $C_{10}H_{11}ClPdS$: C, 39.36; H, 3.63%. MW calcd for the dimer: 610. Found 665 at a concentration of 1.0×10^{-2} M (1 M=1 mol dm^{-3}).

Generation of [Pd(η^3-$CH_2C(CMe_2Cl)CH_2$)(SPh)(PPh_3)]$_2$ (4b). When a mixture of **2b** (5.5 mg, 0.017 mmol) and PPh_3 (4.3 mg, 0.016 mmol) in C_6D_6 (0.6 mL) was monitored by ^{1}H NMR 10 min after mixing the reagents, the quantitative formation of **4b** was confirmed. ^{1}H NMR (C_6D_6) $\delta = 7.95$ (d, $J = 7.3$ Hz, 2H), 7.79 (m, 6H), 6.9—7.1 (m, 12H), 3.35 (m, 1H), 3.34 (s, 1H), 3.11 (d, $J = 10.3$ Hz, 1H), 2.43 (s, 1H), 1.37 (s, 3H), 1.42 (s, 3H). This gradually isomerized to **5b** (almost completely after 4 h).

Synthesis of [Pd{η^3-$CH_2C(CH_2SPh)CH_2$}(Cl)(PPh_3)] (5a). Complex **5a** was given by adding PPh_3 (46 mg, 0.18 mmol) to **3a** (50 mg, 0.16 mmol) in CH_2Cl_2 (5 mL). Recrystallization from CH_2Cl_2/hexane gave yellow crystals of **5a** (70 mg). Yield: 73%. ^{1}H NMR (C_6D_6) $\delta = 7.75$ (m, 8H), 6.8—7.1 (m, 12H), 4.36 (d, $J = 5.4$ Hz, 1H), 3.43 (d, $J = 8.9$ Hz, 1H), 3.04 (s, 2H), 2.47 (br s, 2H). Found: C, 59.61; H, 4.47%. Calcd for $C_{28}H_{26}ClPPdS$: C, 59.27; H, 4.62%.

Synthesis of [Pd{η^3-$CH_2C(CH_2SPh)CMe_2$}(Cl)(PPh_3)] (5b). To a C_6H_6 solution (1 mL) of **2b** (23.4 mg, 0.070 mmol) was added PPh_3 (18.4 mg, 0.070 mmol); the mixture was stirred for 4 h. A yellow solution was concentrated and residual solids were subjected to flash column chromatography (silica gel, CH_2Cl_2 100%), yielding **5b** (R_f 0.08). Recrystallization from C_6H_6/pentane gave yellow crystals of **5b** (14 mg). Yield: 33%. ^{1}H NMR ($CDCl_3$) $\delta = 7.59$ (m, 6H), 7.40 (m, 12H), 7.26 (m, 2H), 3.53 (s, 2H), 2.73 (s, 2H), 1.66 (d, $J = 7.6$ Hz, 3H), 1.45 (d, $J = 5.4$ Hz, 3H). Found: C, 60.55; H, 5.07%. Calcd for $C_{30}H_{30}ClPPdS$: C, 60.51; H, 5.08%.

Synthesis of Phenyl 2-(Phenylthiomethyl)allyl Sulfide (10). An authentic sample of **10** was prepared as follows: to dry MeOH (50 mL) was added Na (0.90 g, 0.039 mmol) and PhSH (3.6 mL, 0.035 mmol). The mixture was stirred for 5 min and 3-chloro-2-chloromethyl-1-propene (2.10 g, 0.017 mmol) was added. After 1 h, the solvent was removed under reduced pressure and the residue was extracted with Et_2O (3×100 mL)/H_2O (100 mL). The combined organic layers were dried over $MgSO_4$ and Et_2O was removed. Distillation of the residue under reduced pressure (2.5 mmHg, 162 °C) (1 mmHg = 133.322 Pa) gave pure **10** (3.66 g). Yield: 76%. ^{1}H NMR ($CDCl_3$) $\delta = 7.1$—7.3 (m, 10H), 4.92 (s, 2H), 3.71 (s, 4H). Found: C, 70.44; H, 6.05%. Calcd for $C_{16}H_{16}S_2$: C, 70.54; H, 5.92%.

Synthesis of [Pd{η^3-$CH_2C(CH_2Cl)CH_2$}(Cl)(PPh_3)] (8a). The treatment of **1a** (617 mg, 2.67 mmol) with PPh_3 (700 mg, 2.67 mmol) in CH_2Cl_2 (5 mL) followed by filtration and recrystallization with CH_2Cl_2/hexane gave crystals of **8a** (1197 mg). Yield: 91%. ^{1}H NMR ($CDCl_3$) $\delta = 7.55$—7.65 (m, 6H), 7.35—7.5 (m, 9H), 4.64 (d, $J = 4.8$ Hz, 1H), 4.08 (d, $J = 12.8$ Hz, 1H), 3.92 (d, $J = 12.8$ Hz, 1H), 3.70 (d, $J = 9.6$ Hz, 1H), 3.03 (s, 1H), 2.86 (s, 1H). Found: C, 53.47; H, 4.39%. Calcd for $C_{22}H_{21}Cl_2PPd$: C, 53.52; H, 4.29%.

Synthesis of [Pd{η^3-$CH_2C(CMe_2Cl)CH_2$}(Cl)(PPh_3)] (8b). This was prepared from **1b** in similar manner to that for **8a**. Yield: 78%. ^{1}H NMR ($CDCl_3$) $\delta = 7.55$—7.7 (m, 6H), 7.35—7.5 (m, 9H), 4.70 (m, 1H), 3.57 (d, $J = 9.7$ Hz, 1H), 3.13 (s, 1H), 2.77 (s, 1H), 1.74 (s, 3H), 1.73 (s, 3H). Found: C, 55.44; H, 4.91%. Calcd for $C_{24}H_{25}Cl_2PPd$: C, 55.25; H, 4.83%.

Synthesis of [Pd{η^3-$CH_2C(CH_2CH{=}CH_2)CH_2$}(Cl)(PPh_3)] (11a). To a CH_2Cl_2 solution of **8a** was added $Bu_3SnCH{=}CH_2$ (85 µL, 0.29 mmol); the mixture was stirred for 8 h. The solvent was removed under reduced pressure, and the residue was washed with hexane repeatedly. Recrystallization from CH_2Cl_2/hexane gave crystals of **11a** (42 mg). Yield: 30%. ^{1}H NMR ($CDCl_3$) $\delta = 7.55$—7.7 (m, 6H), 7.35—7.5 (m, 9H), 5.75 (m, 1H), 5.05 (m, 2H), 4.54 (d, $J = 6.8$ Hz, 1H), 3.63 (d, $J = 9.7$ Hz, 1H), 2.90 (d, $J = 6.8$ Hz, 1H), 2.81 (br s, 3H). Found: C, 59.15; H, 4.94%. Calcd for $C_{24}H_{24}ClPPd$: C, 59.40; H, 4.98%.

Synthesis of [Pd{η^3-$CH_2C(CH_2CH{=}CH_2)CMe_2$}(Cl)($PPh_3$)] (11b). This was prepared from **8b** in a similar manner to that for **11b**. Yield: 25%. ^{1}H NMR ($CDCl_3$) $\delta = 7.65$—7.55 (m, 6H), 7.45—7.3 (m, 9H), 5.71 (m, 1H), 5.00 (m, 1H), 4.95 (t, $J = 1.4$ Hz, 1H), 2.91 (br s, 2H), 2.81 (br s, 2H), 1.86 (d, $J = 8.4$ Hz, 3H), 1.52 (d, $J = 5.9$ Hz, 3H). Found: C, 60.47; H, 5.83%. Calcd for $C_{26}H_{28}ClPPd$: C, 60.83; H, 5.50%.

Crystal Structure Determination. Crystals of **3a** $(CHCl_3)_2$ suitable for a single-crystal X-ray analysis were grown by the slow evaporation of a solution of **3a** in $CHCl_3$ at room temperature. The crystal was sealed in a glass capillary and used for an X-ray experiment. The data were obtained on a Rigaku RAXIS-CS diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The calculation was carried out with the TEXSAN crystallographic software package of Molecular Structure Corp. The structure was solved by a direct method and refined by full-matrix least-squares procedures,

Table 1. Crystal Data for **3a**

Formula	$C_{20}H_{22}Cl_2Pd_2S_2(CHCl_3)_2$
Mol.wt.	849.98
Crystal size/mm	0.2×0.2×0.2
Crystal system	Monoclinic
Space group	$P2_1/c$ (No.14)
a/Å	13.700(3)
b/Å	7.9408(8)
c/Å	15.496(1)
β/°	110.12(1)
V/Å^3	1583.0(4)
Z	2
D_c/g cm^{-3}	1.781
μ(Mo $K\alpha$)/cm^{-1}	19.55
λ (Mo $K\alpha$)/Å	0.71070
F(000)	832.00
Temp/°C	23.0
$2\theta_{max}$/deg	60.1
No. observed data ($I>4.00\sigma(I)$)	2690
R	0.058
R_w	0.112

Table 2. Positional Parameters and Equivalent Isotopic Temperature Factors (B_{eq}) for Non-H Atoms

Atom	x	y	z	B_{eq}/Å^2
Pd(1)	0.01752(5)	−0.20360(7)	−0.00224(4)	3.38(2)
Cl(1)	−0.0729(2)	−0.2607(4)	−0.1607(2)	4.69(5)
S(1)	−0.1587(2)	0.0462(3)	0.0192(1)	3.53(4)
C(1)	−0.0364(8)	−0.2114(9)	0.1124(6)	4.2(2)
C(2)	0.0727(8)	−0.207(1)	0.1445(6)	5.3(2)
C(3)	−0.0845(10)	−0.346(1)	0.0509(8)	5.7(3)
C(4)	−0.1007(7)	−0.070(1)	0.1273(5)	4.0(2)
C(5)	−0.2449(7)	0.183(1)	0.0495(6)	3.9(2)
C(6)	−0.3499(7)	0.158(1)	0.0077(8)	4.9(2)
C(7)	−0.4198(9)	0.264(2)	0.030(1)	6.6(3)
C(8)	−0.3813(9)	0.393(2)	0.0939(8)	6.5(3)
C(9)	−0.2789(8)	0.412(1)	0.1368(7)	5.4(2)
C(10)	−0.2066(7)	0.312(1)	0.1127(6)	4.0(2)

Table 3. Selected Bond Lengths (l) and Bond Angles (θ) of **3a**

Lengths	l/Å	Angles	θ/°
Pd(1)–Cl(1)	2.383(2)	Cl(1)–Pd(1)–S(1)	98.01(8)
Pd(1)–S*(1)	2.392(2)	Cl(1)–Pd(1)–C(1)	130.0(3)
Pd(1)–C(1)	2.15(1)	Cl(1)–Pd(1)–C(2)	164.3(3)
Pd(1)–C(2)	2.136(9)	Cl(1)–Pd(1)–C(3)	96.7(3)
Pd(1)–C(3)	2.17(1)	S*(1)–Pd(1)–C(1)	128.9(2)
S(1)–C(4)	1.837(8)	S*(1)–Pd(1)–C(2)	97.0(3)
S(1)–C(5)	1.78(1)	S(1)–Pd(1)–C(3)	164.9(3)
C(1)–C(2)	1.40(2)	C(2)–Pd(1)–C(3)	68.1(4)
C(1)–C(3)	1.43(1)	Pd(1)–S*(1)–C(4)	104.5(3)
C(1)–C(4)	1.49(1)	Pd(1)–S*(1)–C(5)	110.1(3)
		C(4)–S(1)–C(5)	100.7(4)
		Pd(1)–C(1)–C(2)	70.5(6)
		Pd(1)–C(1)–C(3)	71.5(7)
		Pd(1)–C(1)–C(4)	119.7(6)
		C(2)–C(1)–C(3)	116(1)
		C(2)–C(1)–C(4)	122.8(8)
		C(3)–C(1)–C(4)	120.2(9)
		S(1)–C(4)–C(1)	109.3(6)

the function minimized being $\Sigma w(|F_o|-|F_c|)^2$. The non-hydrogen atoms were refined anisotropically. The crystallographic data, positional parameters and equivalent isotopic temperature factors (B_{eq}) for non-H atoms and selected bond lengths and bond angles are summarized in Tables 1, 2, and 3.

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