Synthesis of η^3-2-stannylmethylallylpalladium complexes and their destannylation leading to trimethylenemethane-palladium species

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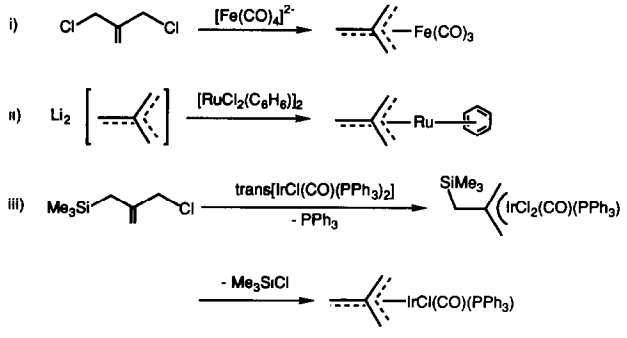
Abstract

η^3-2-Stannylmethylallylpalladium chloride dimer $[Pd(\eta^3\text{-}CH_2C(CH_2SnMe_3)CH_2)Cl]_2$ (**1a**) reacted with a neutral ligand L to form corresponding cationic complexes $[Pd(\eta^3\text{-}CH_2C(CH_2SnMe_3)CH_2)L_2]Cl$ (L = PPh_3: **2a**, 1/2 bipy: **5** (bipy = 2,2′-bipyridyl)), which were characterized by ^1H NMR at low temperature only for **2a** and at room temperature for **5**. On addition of Bu_3SnCl the cationic complex **5** underwent stannyl group exchange equilibrium with $[Pd(\eta^3\text{-}CH_2C(CH_2SnBu_3)CH_2)$ (bipy)]Cl. Addition of 2 equiv PPh_3 and RCHO (R = Ph, CH_2=CH) to **1a** at room temperature afforded the cycloaddition products, methylenetetrahydrofurans, in good yields. The complex **1a** reacted with PhCHO in the presence of bipy and dppe (dppe = 1,2-bis(diphenylphosphino)ethane) to give the aldehyde adduct complexes $[Pd(\eta^3\text{-}CH_2C(CH_2CHPh(OSnMe_3))CH_2)L_2]Cl$ (L = 1/2 bipy, 1/2 dppe), which were characterized by ^1H NMR. The possible generation and the reactivities of the trimethylenemethane-palladium complex intermediate are discussed in the light of these results.

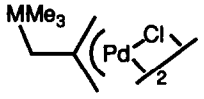
Key words: Palladium; Stannyl; Destannylation; Trimethylenemethane

1. Introduction

Since the isolation of the first trimethylenemethane (TMM) complex $[Fe\{\eta^4\text{-}C(CH_2)_3\}(CO)_3]$ [1], certain TMM complexes have been synthesized via three main routes; (i) dehalogenation of the dihalogen substituted precursor [1], (ii) ligand exchange of the TMM dianion [2] and (iii) desilylation of the η^3-2-silylmethylallyl complex [3].



Attack of the OAc anion at the silyl group similar to the third reaction (iii) has been proposed to play a role in generating a key intermediate, the TMM-Pd complex in Pd-catalyzed [3 + 2] cycloaddition [4]. Synthesis of η^3-2-silylmethylallyl complexes of Pd^{II} and Pt^{II} has been reported briefly [5], but no detailed information on generation of the TMM complex has been available. We have synthesized η^3-2-stannylmethylallyl and η^3-2-silylmethylallylpalladium complexes **1a** and **1b** and examined their reactions with PPh_3 and other ligands leading to liberation of Cl^- ion which is capable of attacking the Sn or the Si atom.



1a: M=Sn
1b: M=Si

2. Results

Treatment of $PdCl_2(PhCN)_2$ with 2-methylene-1,3-propanediylbis(trimethyl(stannane or silane)) in CH_2Cl_2 at room temperature resulted in the formation of

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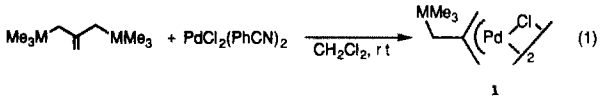
good yields of [η^3-[2-(trimethylstannyl or silyl)methyl] allyl]palladium chloride dimer **1a** or **1b** (eqn. (1)). The complex **1b** was synthesized previously by a different method [6], but the present method gave the better yield. The complexes **1** remained unchanged when allowed to stand in a $CDCl_3$ solution in an NMR tube at room temperature for a day.



(1)

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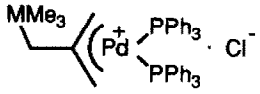
The complexes **1a** and **1b** reacted in $CDCl_3$ with 2 equiv of PPh_3 to form the cationic complexes **2a** and **2b**. The ^1H and ^{31}P NMR spectral data of the silyl analogue **2b** (see Table 1) were almost identical with those of [Pd(η^3-$CH_2C(CH_2SiMe_3)CH_2$)(PPh_3)$_2$]ClO_4 which was generated by treatment of **2b** with $AgClO_4$. The complex **2b** was stable in $CDCl_3$ solution in an NMR tube at room temperature. Furthermore, **2b** did not react with aldehyde at room temperature for 3 days (*cf.* the results with the stannyl analogue **2a** described later). The complex **2b** appeared to be unsuitable for generating the TMM complex.

Table 1
Selected ^1H NMR spectral data of complexes in $CDCl_3$ at 25°C

Complex	Me_3M (J_{SnH})	CH_2 (J_{SnH})	H_{anti}	H_{syn}
1b	0.10	1.90	2.75	3.67
2b [a]	0.03	1.60	3.34	3.48
1a	0.20 (53.5 Hz)	2.08 (58.0 Hz)	2.66	3.62
2a [b]	0.06 (54.6 Hz)	1.79 (57.9 Hz)	3.00	3.31
5	0.18 (53.4 Hz)	2.11 (57.6 Hz)	3.04	3.66
5'	–	2.09 (51.4 Hz)	3.04	3.62

[a] ^{31}P NMR: $\delta = -118.1$ (s). [b] In CD_2Cl_2 at −70°C, ^{31}P NMR: $\delta = -118.9$ (s).



2a: M = Sn
2b: M = Si

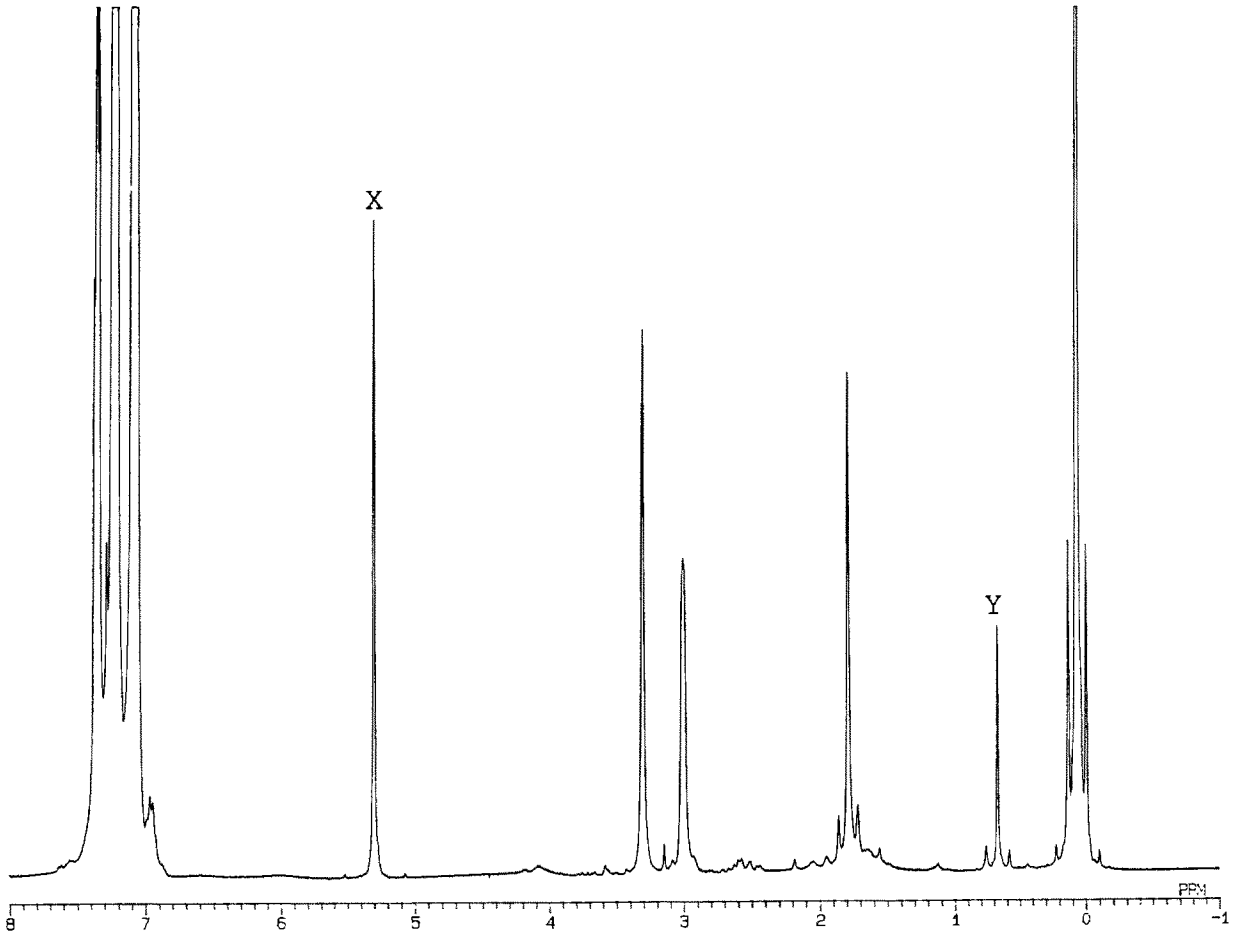
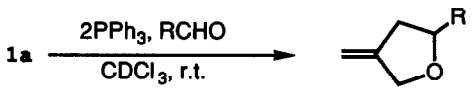


Fig. 1. ^1H NMR spectrum of **2a** generated from **1a** (0.10 mol/l) and PPh_3 (0.20 mol/l) in CD_2Cl_2 at −70°C. X denotes solvent signal, and Y Me_3SnCl signal.

The cationic stannyl analogue **2a** was generated in dry CD_2Cl_2 at $-70°C$ and characterized by ^1H and ^{31}P NMR spectra only at low temperature (Table 1). In ^1H NMR spectra of **2a** (Fig. 1), chemical shifts of the *syn* and *anti* protons are similar to those of **2b**. Also, the chemical shift values and the H–Sn coupling constants for the Me_3Sn and $SnCH_2$ proton signals indicate the presence of the CH_2SnMe_3 skeleton. With the rise of temperature, the cationic complex **2a** began to decompose, resulting in a complicated product mixture. The hoped-for TMM complex was not found in ^1H NMR spectra.

The reaction of the dimeric complex **1a** with 2 equiv. of PPh_3 in the presence of CD_3OD afforded a hydrolysis product $[Pd(\eta^3\text{-}CH_2CMeCH_2](PPh_3)_2]Cl$ **3** [7] in which one of the methyl hydrogens was mostly replaced by deuterium.

The treatment of **1a** and 2 equiv. PPh_3 with aldehydes in $CDCl_3$ gave cycloadducts (substituted methylenetetrahydrofuran **4**) together with **3** (eqn (2)). The formation of **3** may be ascribed to the reaction of the TMM-Pd intermediate with $CHCl_3$ (see Discussion) or the residual H_2O in the solvent. Benzaldehyde and acrolein gave the cycloadducts **4a** and **4b** in moderate yields, but propionaldehyde gave only a small amount of **4c**.



(2)

4a: R = Ph (71%)
4b: R = CH_2=CH (62%)
4c: R = Et (16%)

The dimeric complex **1a** reacted with 1 equiv of bipy in $CDCl_3$ to give the cationic complex **5**, as confirmed by comparison of its ^1H NMR data (Fig. 2, Table 1) with those of $[Pd(\eta^3\text{-}CH_2C(CH_2SnMe_3)CH_2)(bipy)]ClO_4$. Attempts to isolate **5** failed owing to its great sensitivity to water.

Addition of Bu_3SnCl to the cationic complex **5** resulted in the attainment of an equilibrium between the cationic complexes **5** and **5'** (Scheme 1). The equi-

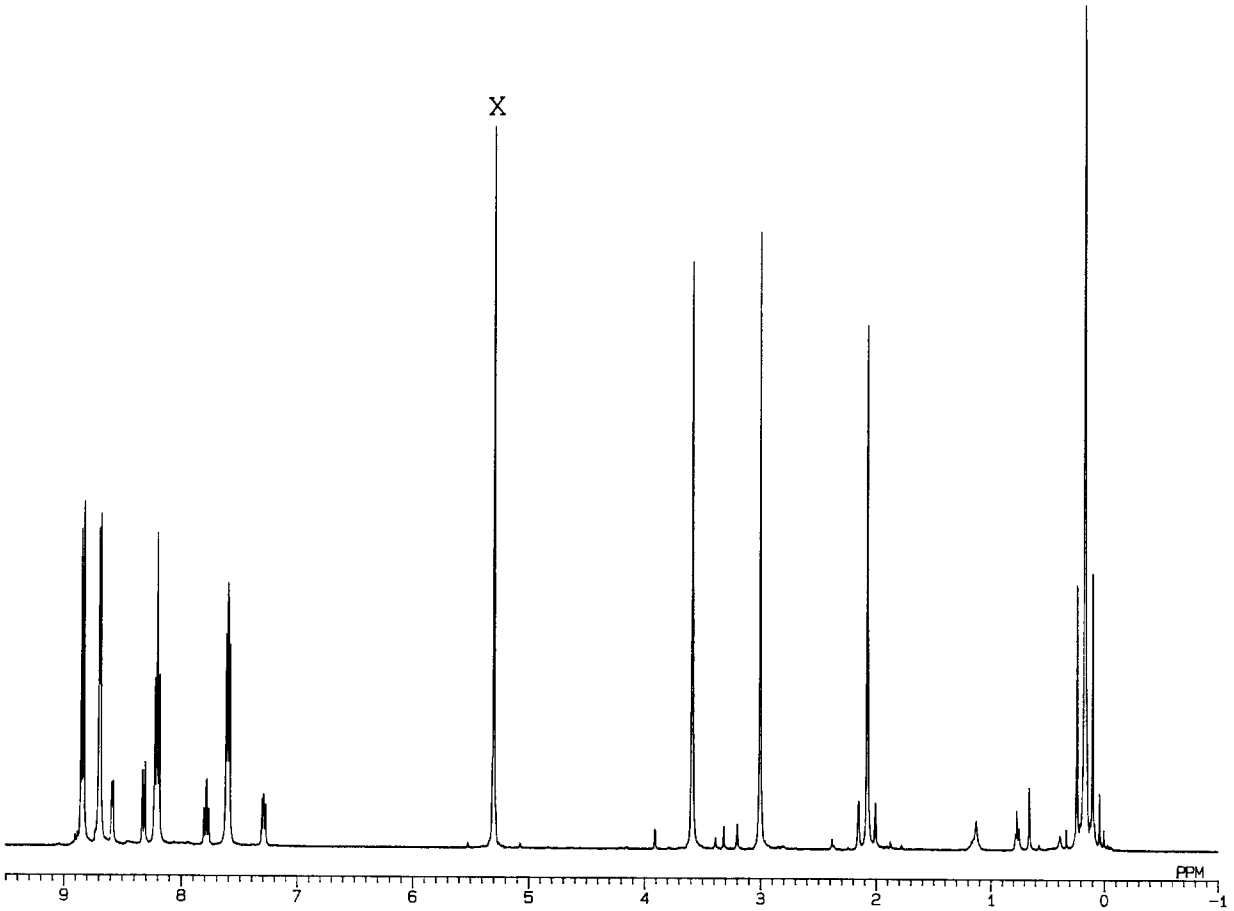
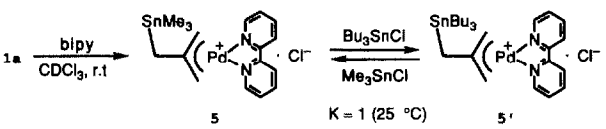
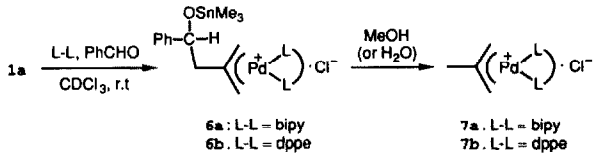


Fig. 2. ^1H NMR spectrum of **5** generated from **1a** (0.05 mol/l) and bipy (0.06 mol/l) in CD_2Cl_2 at $-70°C$. X denotes solvent signal.



Scheme 1.



Scheme 2.

librium constant $K = 1$ was evaluated by comparing the integral values of the *syn* protons of the two complexes. In contrast to these results, addition of Bu_3SnCl to the dimeric complex **1a** led to no exchange of the stannyl groups.

Interestingly, the cationic complex **5** reacted with PhCHO in $CDCl_3$ or CD_2Cl_2 to form the palladium complex **6a** which is the aldehyde adduct of **5** (Scheme 2). The identification of **6a** was made on the basis of ^1H NMR spectra (Fig. 3). The bond formation between the aldehyde carbon and CH_2 is supported by the appearance of $^3J_{HH}$ couplings between the methine and methylene protons whose chemical shifts are similar to those of the cycloadduct **4a**. Furthermore, the α-methylene protons as well as the *anti* and *syn* protons of the η^3-allyl ligand which resonate at reasonable chemical shifts for a cationic η^3-allyl(bipy) complex are all non-equivalent because of the presence of the asymmetric carbon. After 1 day, the complex **6a** disappeared without forming the cycloadduct, and the only product identified was the η^3-2-methylallyl complex **7a**. This complex was also formed rapidly in good yield when methanol was added to the solution of **6a**. Interestingly, the ^1H NMR spectra showed that the methyl group of **7a**, which was obtained by allowing **6a** to stand in $CDCl_3$, contained *ca.* 15% of deuterium (see Experimental section), possibly as the result of the deuterium transfer from $CDCl_3$ to an active intermediate (see later).

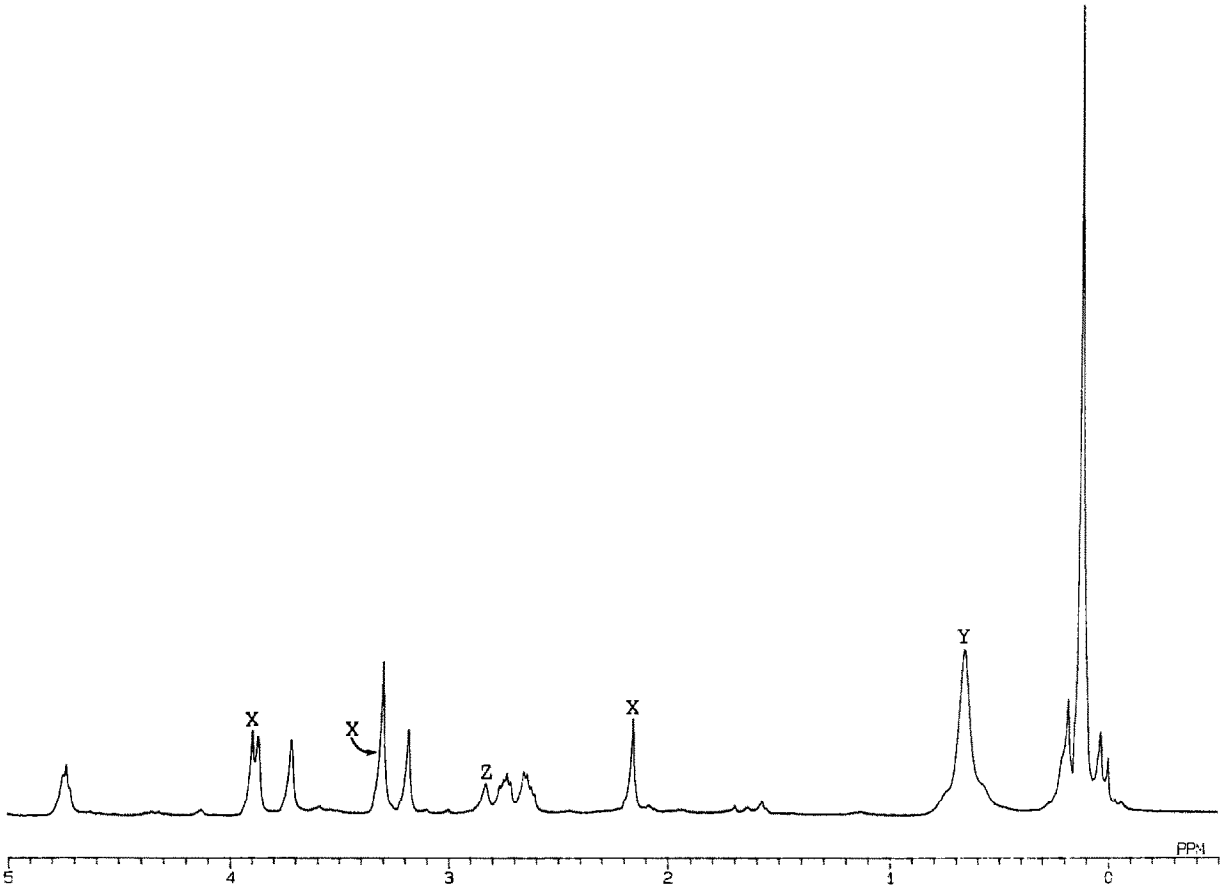
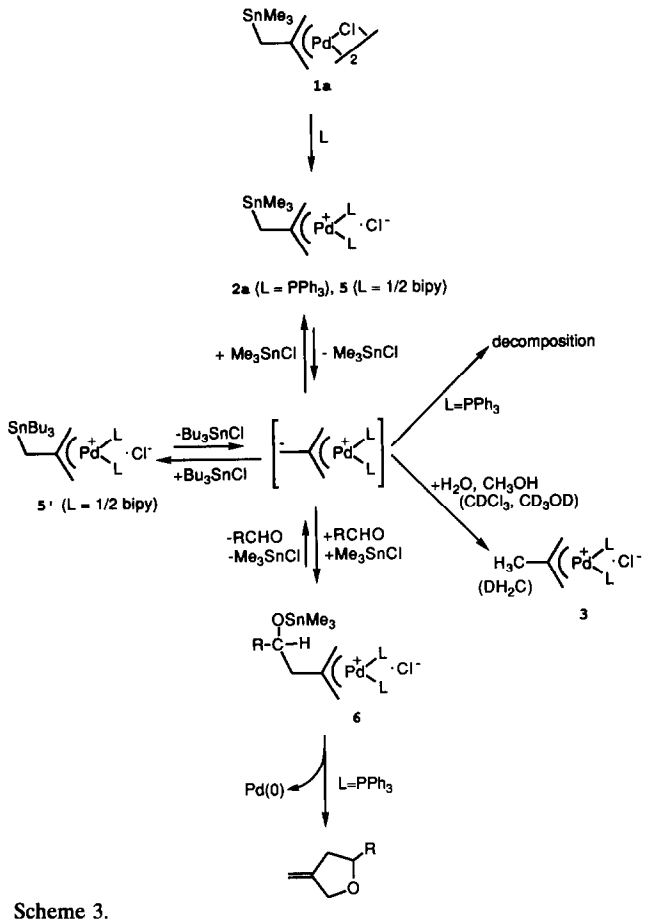


Fig. 3. ^1H NMR spectrum taken at -70°C, of **6a** generated from **1a** (0.07 mol/l), bipy (0.09 mol/l) and PhCHO (0.16 mol/l) in CD_2Cl_2 at 0°C for 3 h. X denotes signals of **7a**, and Y Me_3SnOH signal. Z is an unknown signal.



Scheme 3.

In the case of the reaction of **1a** with dppe, the same results as those with the bipy ligand were obtained (Scheme 2). The mixture of **1a** and dppe reacted with PhCHO to form the aldehyde adduct complex **6b**. After 1 day, the 2-methylallyl complex **7b** containing partially deuterated methyl group was observed. This complex was also formed rapidly when methanol was added to **6b**.

3. Discussion

The results described above may be explained by pathways outlined in Scheme 3. It is presumed that the cationic complexes **2a** and **5** eliminate Me_3SnCl to form the TMM complex. However, this TMM complex rapidly recombines with Me_3SnCl to regenerate the cationic complexes unless quenched by the other electrophiles. For $L = PPh_3$, the TMM complex decomposes irreversibly, possibly because of the ease of PPh_3 dissociation and/or stabilization of a presumed Pd^0 by-product. Besides being quenched by Me_3SnCl, the TMM complex may react with Bu_3SnCl to result in the stannyl group exchange. This intermediate may be quenched not only by methanol or water but by $CHCl_3$ or $CDCl_3$ to give the η^3-2-methylallyl complex. These results indicate the quite high basicity of the TMM complex.

If aldehydes exist in the system, the PPh_3 complex **2a** is converted into the cycloaddition product methylenetetrahydrofuran in moderate yields in the case of benzaldehyde or acrolein. The intermediate aldehyde adduct complexes **6** can be detected for $L = 1/2$ bipy and 1/2 dppe. These adduct complexes **6** did not undergo the cycloaddition, because bipy lacks the ability to stabilize the Pd^0 moiety and dppe does not stabilize the Pd^0 state as effectively as PPh_3 [8]. On the other hand, PPh_3 stabilizes the Pd^0 state sufficiently to facilitate the cycloaddition. The available evidence clearly indicates that the adduct formation from the Pd-TMM intermediate and the aldehyde is a reversible process.

The cationic nature of **2a** and **5** may be an important requirement for the destannylation, for addition of $[Bu_4N]Cl$ to the neutral complex **1a** led to no similar destannylation at all. Finally, it is not certain whether the much lower efficiency of the η^3-2-silylmethylallyl analogue **2b** with respect to the TMM complex formation is due to a thermodynamic or a kinetic factor. The Si–C bond being stronger than the Sn–C bond may contribute to both factors.

4. Experimental details

^1H and ^{31}P NMR spectra were recorded on Bruker AM 600 and JEOL GSX-400 spectrometers as $CDCl_3$ or CH_2Cl_2 solutions with reference to internal $CHCl_3$ ($\delta = 7.27$) or CH_2Cl_2 ($\delta = 5.30$) in ^1H and external $P(OMe)_3$ ($\delta = 0.00$) in ^{31}P NMR. Melting point was determined on a Kyoto Keiryoki Seisakujo micromelting point apparatus and was uncorrected.

Solvents were dried by standard methods and distilled prior to use. All experiments in NMR tubes were carried out under dry Ar.

4.1. Preparation of 2-methylene-1,3-propanediylbis(trimethylsilane)

To a stirred solution of hexamethyldisilane (7.11 g, 48.6 mmol) in THF-HMPA (4:1 170 ml) under dry Ar at 0°C was added methyllithium (1.5 M/hexane 24 ml, 36.0 mmol). The red solution was stirred for 30 min, and treated with a THF (30 ml) solution of 3-chloro-2-chloromethyl-1-propene (2.45 g, 18.8 mmol) at −78°C. After 30 min, THF was removed under reduced pressure, and HMPA was partitioned by extraction with Et_2O (100 ml) and H_2O (100 ml × 6). The organic phase was dried over $MgSO_4$ and Et_2O was removed by evaporation under reduced pressure. The residue

was purified by distillation (68°C, 11 mmHg) as a colourless liquid (1.18 g; 31%). ^{1}H NMR ($CDCl_3$): δ 0.04 (s, 18H, Me_3Si), 1.47 (s, 4H, CH_2SiMe_3), 4.37 (s, 2H, CH_2=C).

4.2. Preparation of [Pd(η^3-$CH_2C(CH_2SnMe_3)CH_2$)Cl]$_2$ (1a)

To a stirred CH_2Cl_2 solution (10 ml) of $PdCl_2(PhCN)_2$ (504 mg, 1.31 mmol) was added dropwise 2-methylene-1,3-propanediylbis(trimethylstannane) [9] (520 mg, 1.36 mmol) at room temperature. The solution was stirred for 3 min and the solvent was removed under reduced pressure. The residue was washed with n-hexane and was recrystallized from CH_2Cl_2/n-hexane, giving 357 mg of **1a** (76%). mp. 125°C dec. Calcd for $C_7H_{15}ClPdSn$: C, 23.37; H, 4.20. Found: C, 23.66; H, 4.18%.

4.3. Preparation of [Pd(η^3-$CH_2C(CH_2SiMe_3)CH_2$)Cl]$_2$ (1b)

To a stirred CH_2Cl_2 solution (10 ml) of $PdCl_2(PhCN)_2$ (890 mg, 2.32 mmol) was added dropwise 2-methylene-1,3-propanediylbis(trimethylsilane) (539 mg, 2.69 mmol) at room temperature. The solution was stirred for 2.5 h and the solvent was removed under reduced pressure. The residue was washed with n-hexane, giving 478 mg of **1b** (77%). The ^{1}H NMR data were identical with those reported [6].

4.4. NMR characterization of 2b and 5

The ^{1}H and ^{31}P NMR spectral data of **2b** (Table 1) were almost identical with those of [Pd(η^3-$CH_2C(CH_2SiMe_3)CH_2$)(PPh_3)$_2$]ClO_4 which was obtained by treatment of **2b** with $AgClO_4$. ^{1}H NMR ($CDCl_3$) data for [Pd(η^3-$CH_2C(CH_2SiMe_3)CH_2$)(PPh_3)$_2$]ClO_4: δ 0.00 (s, 9H, Me_3Si), 1.49 (s, 2H, CH_2), 3.39 (s, 2H, H_{anti}), 3.58 (s, 2H, J_{PH} = 5.6 Hz, H_{syn}). ^{31}P NMR ($CDCl_3$): δ −117.0 (s). Calcd for $C_{43}H_{45}ClO_4P_2PdSi$: C, 60.02; H, 5.29. Found: C, 60.79; H, 5.65%. Similarly, the spectral data of **5** (Table 1) were close to those of [Pd(η^3-$CH_2C(CH_2SnMe_3)CH_2$)(bipy)]ClO_4. ^{1}H NMR (CD_2Cl_2, −70°): δ 0.16 (s, 9H, J_{SnH} = 55.4 Hz, Me_3Sn), 2.09 (s, 2H, J_{SnH} = 58.3 Hz, CH_2SnMe_3), 3.01 (s, 2H, H_{anti}), 3.62 (s, 2H, H_{syn}).

4.5. Reaction of 1a with CD_3OD in the presence of PPh_3

To **1a** (5.1 mg, 0.014 mmol) and PPh_3 (7.3 mg, 0.028 mmol) in an NMR tube was added CD_3OD (0.3 ml) and $CDCl_3$ (0.3 ml). ^{1}H NMR examination showed quantitative formation of [Pd(η^3-$CH_2C(CH_2D)CH_2$)Cl(PPh_3)$_2$. ^{1}H NMR ($CDCl_3$): δ 1.97 (1:1:1 triplet, 2H, J_{HD} = 1.9 Hz, CH_2D), 3.45 (s, 2H, H_{anti}), 3.72 (s, 2H, H_{syn}).

4.6. Cycloaddition of 1a with PhCHO in the presence of PPh_3

To **1a** (8.0 mg, 0.022 mmol) and PPh_3 (12.4 mg, 0.047 mmol) in an NMR tube was added a $CDCl_3$ solution of PhCHO (0.079 M/$CDCl_3$ 0.6 ml, 0.47 mmol) which had been dried over active molecular sieves 3A prior to the reaction. ^{1}H NMR examination showed formation of 4-methylene-2-phenyl-tetrahydrofuran **4a** (71% based on the Me_3Sn signals as an internal reference) together with 18% of **3**. ^{1}H NMR ($CDCl_3$) data for **4a**: δ 2.58 (ddd, 1H, J = 2.3, 8.8, 15.8 Hz, CH_2CPh), 2.96 (dd, 1H, J = 6.4, 15.8 Hz, CH_2CPh), 4.41 (dd, 1H, J = 2.3, 13.5 Hz, CH_2O), 4.59 (d, 1H, J = 13.5 Hz, CH_2O), 4.97 (dd, 1H, J = 2.2, 2.3 Hz, C=CH_2), 4.98 (dd, 1H, J = 6.4, 8.8 Hz, CHPh), 5.04 (dd, 1H, J = 2.2, 2.3 Hz, C=CH_2), 7.2–7.3 (m, 5H, Ph). These ^{1}H NMR data were almost identical with those reported [10].

4.7. Cycloaddition of 1a with CH_2=CHCHO in the presence of PPh_3

To **1a** (6.7 mg, 0.019 mmol) and PPh_3 (10.0 mg, 0.038 mmol) in an NMR tube was added CH_2=CHCHO (2.5 ml, 0.037 mmol) and dry $CDCl_3$ (0.6 ml). CH_2=CHCHO was distilled from $CaSO_4$ prior to use. ^{1}H NMR examination showed formation of 4-methylene-2-vinyl-tetrahydrofuran (**4b**) (62%) together with 36% of **3**. ^{1}H NMR ($CDCl_3$) data for **4b**: δ 2.37 (ddd, 1H, J = 2.2, 8.2, 15.6 Hz, CCH_2C=C), 2.71 (dd, 1H, J = 8.2, 15.6 Hz, CCH_2C=C), 4.28 (dd, 1H, J = 2.3, 13.0 Hz, OCH_2C=C), 4.39–4.43 (m, 2H, $OCHC_2$ and OCH_2C=C), 4.92 (dd, 1H, J = 2.1, 2.2 Hz, CH_2=CC_2), 5.00 (dd, 1H, J = 2.2, 2.2 Hz, CH_2=CC_2), 5.16 (d, 1H, J = 10.4 Hz, CH_2=CHC), 5.29 (d, 1H, J = 17.3 Hz, CH_2=CHC), 5.89 (ddd, 1H, J = 6.3, 10.4, 17.3 Hz, CH_2=CHC).

4.8. Cycloaddition of 1a with EtCHO in the presence of PPh_3

To **1a** (4.9 mg, 0.014 mmol) and PPh_3 (7.2 mg, 0.020 mmol) in an NMR tube was added EtCHO (1.0 ml, 0.020 mmol) and dry $CDCl_3$ (0.6 ml). EtCHO was distilled from $CaCl_2$ prior to use. ^{1}H NMR examination showed formation of 4-methylene-2-ethyl-tetrahydrofuran (**4c**) (18%) together with 25% of **3**. ^{1}H NMR ($CDCl_3$) data for **4c**: δ 0.96 (t, J = 7.5 Hz, 3H, CH_3), 1.53 (m, 1H, CH_2CH_3), 1.68 (m, 1H, CH_2CH_3), 2.20 (m, 1H, CCH_2C=CH_2), 2.63 (dd, J = 5.9, 15.9 Hz, 1H, CCH_2C=CH_2), 3.86 (m, 1H, OCHEt), 4.23 (dd, J = 1.9, 12.9 Hz, 1H, OCH_2C) 4.38 (d, J = 12.9 Hz, 1H, OCH_2C), 4.90 (t, J = 1.9 Hz, 1H, CH_2=CC_2), 4.97 (dd, J = 1.9, 2.3 Hz, 1H, CH_2=CC_2).

4.9. Reaction of 1a with PhCHO in the presence of bipy

To **1a** (7.4 mg, 0.021 mmol) and bipy (3.2 mg, 0.020 mmol) in an NMR tube was added a $CDCl_3$ solution of PhCHO (0.069 M/$CDCl_3$ 0.6 ml, 0.41 mmol) which had been dried over active molecular sieves 3A prior to the reaction. The formation of **6a** was deduced by ^1H NMR examination. ^1H NMR ($CDCl_3$) data for **6a**: δ 0.26 (s, 9H, J_{SnH} = 53.1 Hz, $OSnMe_3$), 2.75 (dd, 1H, J = 5.6, 13.7 Hz, PhCCH_2), 2.86 (dd, 1H, J = 6.9, 13.7 Hz, PhCCH_2), 3.31 (s, 1H, H_{anti}), 3.37 (s, 1H, H_{anti}), 3.90 (s, 1H, H_{syn}), 3.96 (s, 1H, H_{syn}), 4.87 (dd, 1H, J = 5.6, 6.9 Hz, PhCH). After 1 day methylallyl complex **7a** which contained [Pd(η^3-CH_2S-C(CH_2D)CH_2)(bipy)]Cl was found. On addition of CD_3OD to **6a**, the same result was obtained. ^1H NMR data for **7a**: δ 2.25 (s, CH_3), 2.23 (1:1:1 triplet, J_{HD} = 2.0 Hz, CH_2D), 3.37 (s, 2H, H_{anti}), 3.99 (s, 2H, H_{syn}). These ^1H NMR data were identical with those of [Pd(η^3-CH_2CMe-CH_2)(bipy)]Cl which was generated by treatment of [Pd(η^3-CH_2CMeCH_2)Cl]$_2$ with bipy.

4.10. Reaction of 1a with PhCHO in the presence of dppe

To **1a** (7.6 mg, 0.021 mmol) and dppe (3.2 mg, 0.020 mmol) in an NMR tube was added a $CDCl_3$ solution of PhCHO (0.069 M/$CDCl_3$ 0.6 ml, 0.41 mmol) which had been dried over active molecular sieves 3A prior to the reaction. The formation of **6b** was deduced by ^1H NMR examination. ^1H NMR ($CDCl_3$) data for **6b**: δ 0.26 (br, 9H, $OSnMe_3$), 2.25 (dd, 1H, J = 5.7, 12.2 Hz, PhCCH_2), 2.38 (dd, 1H, J = 7.2, 12.2 Hz, PhCCH_2), 3.08 (br s, 1H, H_{anti}), 3.20 (br s, 1H, H_{anti}), 4.36 (br s, 1H, H_{syn}), 4.65 (br s, 1H, H_{syn}), 4.80 (dd, 1H, J = 5.7, 7.2 Hz, PhCH). After 1 day methylallyl complex **7b** which contained [Pd(η^3-CH_2C(CH_2D)CH_2)(dppe)]Cl was found. On addition of CD_3OD to **6b**, the same result was obtained. ^1H NMR ($CDCl_3$) data for **7b**: δ 1.96 (s, CH_3), 1.94 (1:1:1 triplet, J_{HD} = 2.0 Hz, CH_2D). The *syn* and *anti* protons of this product as well as the complex generated by treatment of [Pd(η^3-CH_2CMeCH_2)Cl]$_2$ with dppe were too broad to confirm at room temperature. However, at -50°C, the *syn* and *anti* protons appeared at δ 3.16 (br s, 2H, J_{PH} = 5.0 Hz, H_{anti}) and 4.68 (br s, 2H, H_{syn}).

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