Studies on Synthesis, Structure, and Reactivity of Mono and Dinuclear η^3-Allenyl/Propargylpalladium Complexes

Ken Tsutsumi

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単核及び複核η^3-アレニル／プロパルギルパラジウム錯体の
合成、構造、及び反応性に関する研究

2000

Ken Tsutsumi

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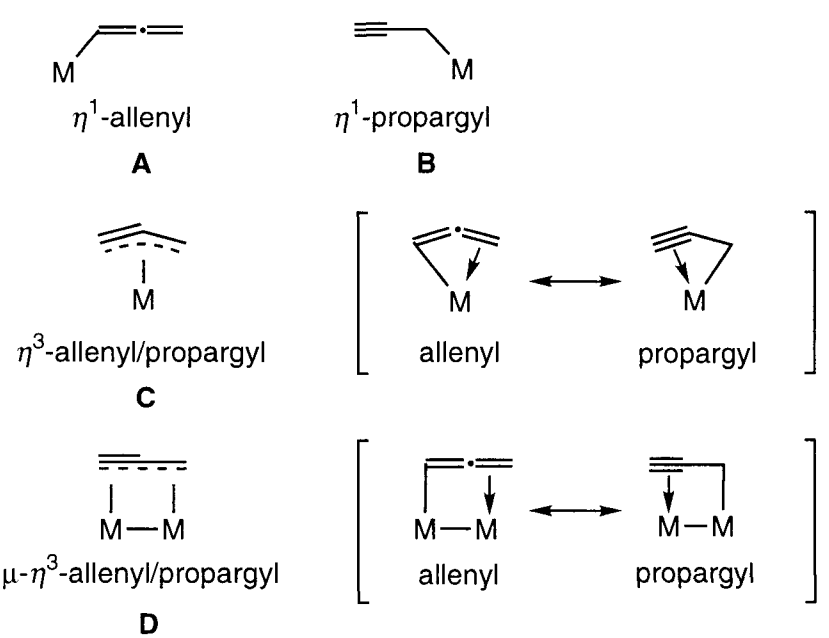
General Introduction

Mono and polynuclear transition-metal complexes bearing hydrocarbyl ligands have been regarded as the key species in synthetic and material chemistry. Transition-metal complexes bearing η^3-allyl ligands have been well investigated over the past few decades, since they have a rich and variable chemistry in their syntheses, structures, and reactivities.[1] The theoretical explorations also increased with regard to many useful organic reactions of allyl compounds, especially those of palladium.[2] Recently, increasing attention has also been paid to allenyl/propargyl transition metal complexes because of their unique bonding mode and reactivity,[3] but much less fundamental aspects have been elucidated in contrast to analogous allyl complexes. Examples of typical bonding modes are presented in Scheme 1. The η^1-bonding allenyl (A) and propargyl (B) complexes have been well studied,[4] compared with η^3-allenyl/propargyl ones (C) (D). The bonding in η^3-allenyl/propargyl complexes can be described in term of two resonance structures: the η^3-allenyl structure and the η^3-propargyl structure.

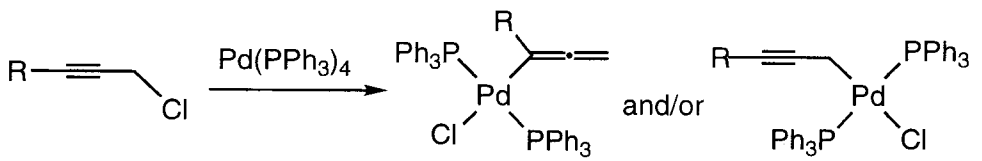
Scheme 1



In spite of many useful catalytic reactions of propargylic and allenylic substrates,[5]

systematic studies of mononuclear and dinuclear complexes containing an allenyl/propargyl ligand, especially those of palladium, have been still limited. The first propargyl- and allenylpalladium complexes prepared by conventional oxidative addition of propargyl or allenyl halides to $Pd(PPh_3)_4$ were of the η^1-bonding type (Scheme 2),[6] which have long been assumed to play a crucial role in the catalytic cycles.

Scheme 2



I planned to prepare a series of cationic and neutral monopalladium complexes of type C in the hope of finding out unique properties inherent in the strained η^3-allenyl/propargyl ligand, and applying these complexes as the intermediate of catalytic reactions. I was also interested in type D complexes because, considering that geometrically linear unsaturated hydrocarbon ligands might match to a linear dinuclear moiety more than to a mononuclear moiety, μ-η^3-allenyl/propargyldipalladiums may be a suitable model to discuss about the metal surface-hydrocarbon interaction of heterogeneous catalytic reaction. I wish to report here in the synthesis, structure and reactivity of type C, cationic (Chapter 1) and neutral (Chapter 2), and type D (Chapter 3) complexes of Palladium which have bearings with organic synthesis using of homogeneous and heterogeneous palladium catalysts.

References

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(2) Abel, E. W.; Stone, F. G. A.; Wilkinson, G. Hegedus, L. S. *Comprehensive Organometallic Chemistry II, Vol. 12*, Elsevier Science Ltd., 1995; Chapter 8.

(3) (a) Doherty, S.; Corrigan, J. F.; Carty, A. J.; Sappa, E. *Adv. Organomet. Chem.*, **1995**, *37*, 39. (b) Wojcicki, A. *New. J. Chem.*, **1994**, *18*, 61. (c) Wojcicki, A.; Shuchart, C. E. *Coord. Chem. Rev.*, **1990**, 35.

(4) Welker, M. E. *Chem. Rev.*, **1992**, *92*, 97 and references cited therein.

(5) (a) Tsuji, J.; Mandai, T. *Angew. Chem., Int. Ed. Engl.*, **1995**, *34*, 2589. (b) Tsuji, J. *Palladium Reagents and Catalysts*, Wiley, Chichester, 1995, pp. 453- 471. (c) Minami, I.; Yuhara, M.; Watanabe, H.; Tsuji, J. *J. Organomet. Chem.*, **1987**, *334*, 225 and references cited therein.

(6) (a) Elsevier, C. J.; Kleijn, H.; Ruitenberg, K.; Vermeer, P. *J. Chem. Soc., Chem. Commun.*, **1983**, 1529. (b) Elsevier, C. J.; Kleijn, H.; Boersma, J.; Vermeer, P. *Organometallics*, **1986**, *5*, 716.

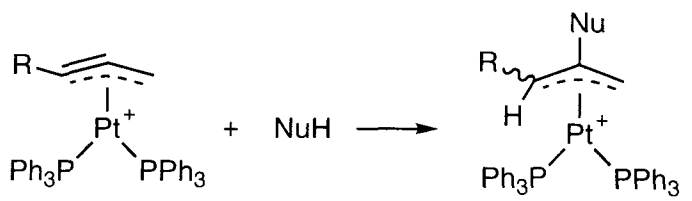
Chapter 1

Cationic η^3-allenyl/propargylpalladium complexes

1-1 Introduction

Recently, transition-metal complexes containing η^3-allenyl/propargyl ligands have been attracting great attention because of their unique structures and reactivities. In 1991, Krivykh reported the synthesis of cationic η^3-allenyl/propargylmolybdenum complex,[1a] which was the first compound containing η^3-allenyl/propargyl ligand. Since this report, cationic type complexes have been investigated on the other metals, such as W,[1b] Re,[1b,c] Pt,[1d,e,f,g] and Pd.[1g] The reactivities of these complexes have been explored to reveal some unique patterns of reactivity. For example, the nucleophilic addition occurred at the central carbon of the η^3-allenyl/propargyl ligand.[1a,c,d,e,g] The most extensively studied reactions of the η^3-allenyl/propargyl complexes have been those of platinum,[1d,e,g] and a generalized reaction is provided in Scheme 1. The reaction of cationic η^3-allenyl/propargylplatinum complexes proceeds by addition of the nucleophile at the central carbon atom and transfer of a hydrogen to the terminal CR carbon atom to afford the η^3-allylplatinum ones under mild condition. Furthermore the MO calculation on the η^3-allenyl/propargylplatinum complex is consistent with the observation.[2] The high reactivity of this type of complex is unique and different from that of η^1-allenyl or η^1-propargyl complexes.[3]

Scheme 1

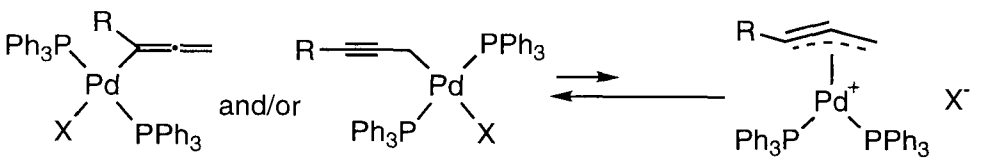


NuH: MeOH, Et_2NH

Cationic η^3-propargyl complexes are expected as a more effective intermediate than neutral η^1-allenyl- and η^1-propargyl complexes in certain catalytic reactions of allenylic or propargylic substrates. Tsuji and co-workers reported many useful palladium catalyzed

reactions of propargylic or allenylic substrates,[4] but η^1-allenyl- and η^1-propargyl complexes have been assumed to play a crucial role in the above catalytic reactions. In view of the analogy with η^3-allylpalladium chemistry, I expected the equilibrium between cationic η^3-allenyl/propargyl and η^1-allenyl and η^1-propargylpalladium complexes may also exist in solution (Scheme 2), and the former might have a role in catalysis more significant than has been assumed before.

Scheme 2

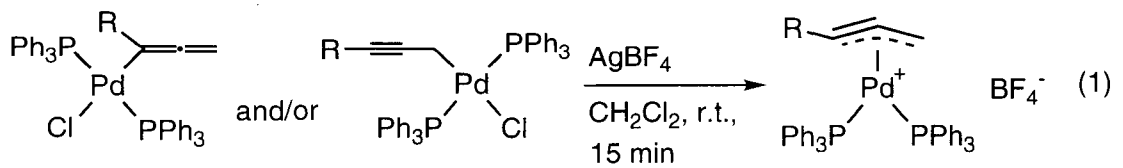


In this chapter, I describe the synthesis, structure and reactivity of some cationic η^3-propargylpalladium complexes. I also examined trends of η^1-η^3 equilibrium of propargyl ligand as a function of the nature of propargyl group, ligand (X), phosphine, and solvent. I will discuss the possibility of these complexes as a catalytic intermediate.

1-2 Synthesis and property of cationic η^3-allenyl/propargylpalladium complexes

Cationic η^3-propargylpalladium complexes **2a, 2b** were prepared by treating η^1-allenyl- and η^1-propargylbis(triphenylphosphine)palladium(II) chloride (**1a**, **1b**)[5] with $AgBF_4$ (eq. 1) in high yields. The η^3-coordination mode in **2a** was established by NMR experiments. Thus, in the ^{13}C NMR spectrum of **2a** in $CDCl_3$, resonances of η^3-allenyl/propargyl carbons at both terminal positions showed large carbon-phosphorus couplings (δ 52.40, dd, J_{PC} = 39.1, 6.2 Hz, CCH_2; δ 104.74, d, J_{PC} = 40.4 Hz, Si*C*C). Moreover, the resonance due to the central carbon of the propargyl group showed two small carbon-phosphorus couplings (δ 113.84, dd, J_{PC} = 8.1, 8.1 Hz). Furthermore, the ^{31}P NMR resonances of two non-equivalent PPh_3 ligands showed phosphorus-phosphorus coupling (J_{PP} = 46.4 Hz). These features are all similar to those of **2b** of which X-ray

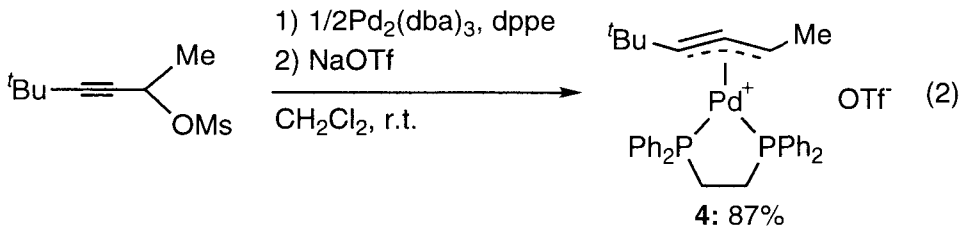
structure determination will be described later, suggesting η^3-coordination of $Me_3SiCCCH_2$ ligand in **2a**.



1a: R = $SiMe_3$ (propargyl)
1b: R = Ph (allenyl:propargyl = 75:25)

2a: 88%
2b: 94%

The preparation of another complex **4** was successful in good yield by the reaction of propargyl mesylate ^{t}BuC≡CCH(Me)OSO_2Me (**3**) with $Pd_2(dba)_3{\cdot}CHCl_3$, dppe (1, 2-bis(diphenylphosphino)ethane), and NaOTf (Tf = SO_2CF_3) (eq. 2).[6] In this reaction, the mesyl group (OSO_2Me) was a more efficient leaving one than halides, and was replaced by the OTf^- ion after oxidative addition. In the ^{13}C NMR spectrum of **4**, the resonances of propargyl terminal carbons showed large carbon-phosphorus coupling (J_{PC} = 37.6, 34.6 Hz) and the ^{31}P resonances of dppe ligands showed two signals at δ 54.90 and 56.00 with P-P coupling, which are similar to those of **2a** and **2b**. The ^1H NMR spectrum of **4** showed the methine proton resonance at δ 4.30. The methine and methyl proton resonances have large proton-phosphorus coupling (J_{PH} = 7.1, 8.8 Hz respectively; established by homonuclear decoupling experiments).

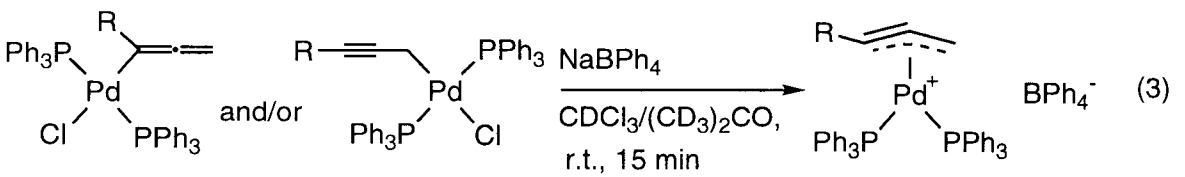


4: 87%

Surprisingly, the cationic η^3-propargylpalladium complexes prepared in this study did not react with methanol and ethanol at all,[7] in contrast to reactions of the corresponding platinum complexes with alcohol, which afforded η^3-2-alkoxyallylplatinum complexes.[1d,e,g] The difference in the reactivity toward the alcohol, between Pd and Pt analogs might reflect a different stability of a possible intermediate, 3-alkoxy-1-metalla-2-cyclobutene (Pt intermediate being more stable than Pd analog) generated by a nucleophilic

attack of an alkoxy group at the central carbon of the η^3-propargyl ligand, which subsequently undergoes protonation to give the η^3-2-alkoxyallyl complex. This explanation is consistent with a proposed origin of a unique metal effect in comparison of the bonding aspect of the metalla-3-cyclobutanone complex[8] between the Pd and Pt ones; the Pt atom stabilizes a metallacyclobutane framework more effectively by a resonance structure than the Pd atom does.

Complexes **1a** and **1b** also reacted with $NaBPh_4$ to give the corresponding cationic η^3-propargylpalladium complexes (**5a**, **5b**), respectively (eq. 3). Although these complexes gradually decomposed in solution, their quantitative formation in the early stage of the reaction was confirmed by ^1H NMR spectra (**5a**: δ CH_2 = 2.99 ppm, J_{PH} = 7.8 Hz, **5b**: δ CH_2 = 3.15 ppm, J_{PH} = 7.8 Hz). Complex **5a** afforded $Me_3SiC{\equiv}CCH_2Ph$ (30%) and $Me_3Si(Ph)C{=}C{=}CH_2$ (3%) in solution after 4 h at room temperature. On the other hand, the corresponding platinum complex, *cis*- and *trans*-Pt(η^1-$CH_2C{\equiv}CPh$)(Cl)(PPh_3)$_2$, did not react with $NaBPh_4$ under the same conditions at all, which strongly suggests that the Pd atom favors the η^3-mode coordination of the allenyl or propargyl ligand more than the Pt atom does.



(3)

1a: R = $SiMe_3$ (propargyl)
1b: R = Ph (allenyl:propargyl = 75:25)

5a: 100%
5b: 100%

The occurrence of the reaction shown in eq. 3 suggests pre-equilibrium between the η^1- and η^3-complexes involving dissociation of the chloride ion in solution (Scheme 2), similar to the known behavior of the η^3-allylpalladium complexes.[9] Although the spontaneous formation of the cationic species from **1a** and **1b** could not be detected spectroscopically, a suitable choice of both the propargyl and phosphine ligands enabled direct observations of the cationic η^3-propargylpalladium complexes with the liberation of the chloride ion as an equilibrating species (see Chapter 1-4).

1-3 X-ray structure of cationic η^3-allenyl/propargylpalladium complex

The molecular structure of **2b** was determined by X-ray diffraction technique (Figure 1). η^3-Allenyl/propargyl group is not linear (C1-C2-C3 = 154(1)°), and palladium, phosphorus and η^3-allenyl/propargyl carbons are located almost on the same plane (dihedral angle between Pd-P1-P2 and C1-C2-C3 = 4.82°). The C1-C2 and C2-C3 bond lengths are 1.22(2) Å and 1.38(2) Å respectively, which indicates that there is considerable contribution of both allenyl and propargyl presentations to this structure. This structure is quite similar to that of the platinum analog,[1e] namely the degree of skeletal strain of the allenyl/propargyl ligand appears to be comparable in the two complexes.

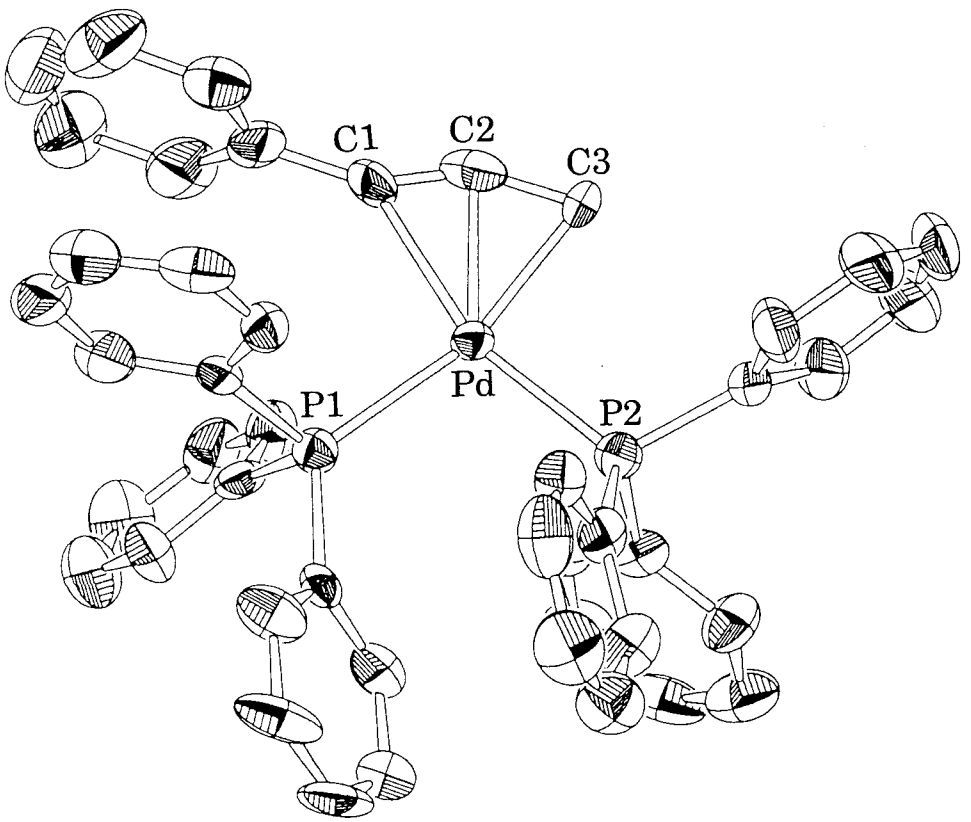


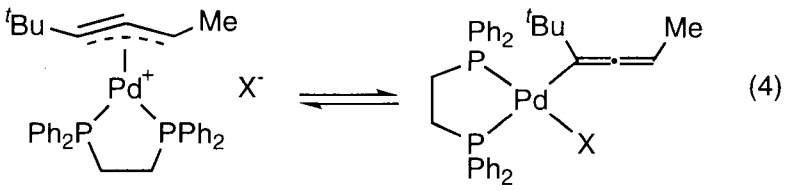
Figure 1. Molecular structure of **2b**. Selected bond distances (Å): Pd-P1 = 2.337(4), Pd-P2 = 2.292(4), Pd-C1= 2.33(2), Pd-C2 = 2.15(2), Pd-C3 = 2.16(2), C1-C2 = 1.22(2), C2-C3 = 1.38(2). Selected angle (deg): C1-C2-C3 = 154(1). Dihedral angles (deg): Pd-P1-P2, C1-C2-C3 = 4.82, Pd-P1-P2, Pd-C1-C3 = 2.38

1-4 Cationic η^3-allenyl/propargylpalladium complex formation in solution

The reaction of ^{t}BuC≡CCH(Me)Cl (**6a**) with a half molar amount of $Pd_2(dba)_3 \cdot CHCl_3$ and an equimolar amount of dppe gave an equilibrium mixture of cationic η^3-propargyl and neutral η^1-allenyl complexes **7a** and **8a** (eq. 4). These complexes were generated only in NMR tubes due to gradual decomposition via β-hydrogen elimination (see later). The ^{1}H NMR data of **7a** are very similar to those of the triflate **4**. Upon forming the η^1-allenyl bond in **8a**, the signals of the methyl and methine protons at the allenyl terminus in **7a** (δ 1.07, 4.25) moved to the higher magnetic field (δ 0.57, 3.01); in particular, the signal of **8a** at δ 3.01 is close to that of the authentic η^1-allenyl complex (**1b**; δ 3.53), but far from that of the η^1-propargyl one (**1b**; δ 1.54).

The equilibrium ratio of **7a** and **8a** was dependent on the nature of the solvent used. In $CDCl_3$, they exist as a mixture of a ratio of 75/25 with the mutual interconversion being slower than the NMR time scale (25 °C). The ratio of **7a** and **8a** changed from 89/11 in DMF-d_7 (run 2) to 0/100 in C_6D_6 (run 3) depending on the solvent used, which indicates that cationic complex **7a** tends to be generated more easily in a polar solvent.

When ^{t}BuC≡CCH(Me)Br **6b** was used as a ligand instead of **6a**, the ratio of **7** and **8** changed from 75/25 (run 1) to 68/32 (run 4) in $CDCl_3$.[10] The equilibrium lies in favor of the cationic η^3-propargyl form by using **6a** instead of **6b**, which is consistent with the order of the leaving group ability from a metal center.[11a] Considering that soft metals, such as Pd(II), have strong affinity for soft ligands,[11b] **8b** containing the Pd-Br bond might be more stable than **8a** containing the Pd-Cl one.



(4)

7a: X = Cl
7b: X = Br

8a
8b

run	X	solvent	**7**/**8**[a]
1	Cl	$CDCl_3$	75/25
2	Cl	DMF-d_7	89/11
3	Cl	C_6D_6	0/100
4	Br	$CDCl_3$	68/32

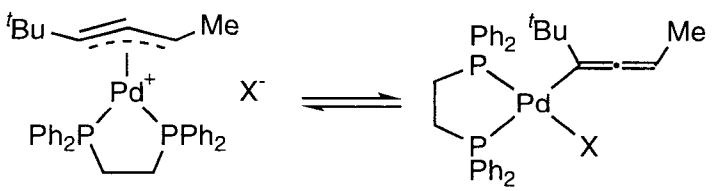
[a] Ratios of **7** and **8** calculated by integrations of respective ^{1}H NMR signals at 25 °C.

In the reaction of $Pd(PPh_3)_4$ with **6a**, only η^1-allenyl complex, *trans*-Pd(η^1-C(Bu^t)=C=CH(Me))(Cl)$(PPh_3)_2$ (**9**), was obtained in either $CDCl_3$ or DMF-d_7. The chemical shift value of the methine proton in ^{1}H NMR spectrum of **9** at δ 3.08 ppm is very close to that of **8a** at δ 3.01 in $CDCl_3$. The reaction of ^{t}BuC≡CCH$_2$Cl (**6c**), instead of **6a**, with Pd(dppe) generated from a half molar amount of $Pd_2(dba)_3$·$CHCl_3$ and an equimolar amount of dppe gave the η^1-propargyl complex Pd(η^1-CH$_2$C≡CBu^t)(Cl)(dppe) (**10**), as a sole product in either $CDCl_3$ or DMF-d_7. The chemical shift value of the methylene protons in the ^{1}H NMR spectrum of **10** at 1.26 ppm, which is very similar to that of an analogous complex, *trans*-Pd(η^1-CH$_2$C≡CBu^t)(Cl)$(PPh_3)_2$,[5b] reveals the η^1-propargyl coordination mode of **10**. These results suggest that the bidentate ligand (dppe) is more favorable for the η^3-coordination of the propargyl/allenyl ligand than triphenylphosphine. The introduction of the alkyl substituent at the propargylic position causes the η^3-form to become more stable.

In solution **7**, **8**, and **9** gradually decomposed to give ^{t}BuC≡CCH=CH$_2$[12] through β-hydrogen elimination reaction. The β-elimination reaction requires the formation of the η^1-propargylpalladium intermediate which might equilibrate with η^1-allenyl and η^3-

propargyl complexes **7** and **8**.[13]

Tsuji and co-workers reported on the reactions of propargyl carbonates with soft nucleophiles catalyzed by Pd(0) (Scheme 3),[4c,d] in which only the η^1-propargyl and η^1-allenyl species were proposed as catalytic intermediates.[4] In their mechanism, nucleophilic addition occurs first at the central carbon of η^1-allenyl moiety and then at the terminal carbon of the allyl group in the generated η^3-allylpalladium intermediate to afford doubly substituted products (Scheme 4).



(4)

7a: X = Cl
7b: X = Br

8a
8b

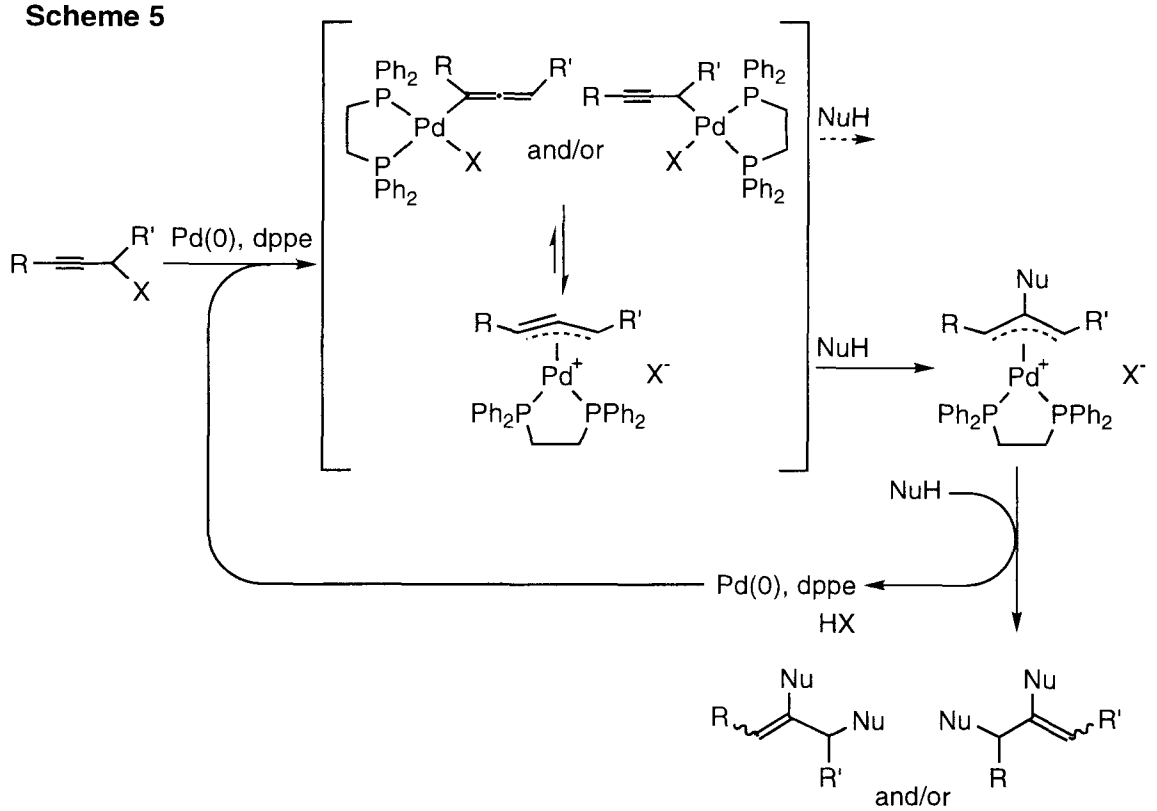
run	X	solvent	**7/8**[a]
1	Cl	$CDCl_3$	75/25
2	Cl	DMF-d_7	89/11
3	Cl	C_6D_6	0/100
4	Br	$CDCl_3$	68/32

[a] Ratios of **7** and **8** calculated by integrations of respective ^{1}H NMR signals at 25 °C.

However, it should be pointed out that the cationic η^3-propargylplatinum and palladium complexes tend to undergo a regioselective nucleophilic reaction at the central carbon atom[1d,e,g] and the η^1-allenyl and propargyl ligands are far less reactive toward nucleophiles than the η^3-propargyl ligand.[14] In fact, Chen indicated that the reaction of the η^1-allenylpalladium complex with $NaCH(CO_2Me)_2$ proceeded via the cationic η^3-propargylpalladium complex as an equilibrium isomer.[3] Moreover, it was found that in the catalytic reactions bidentate ligands, such as dppe and dppp, were more effective than monodentate ligands.[4a] In view of these reactivity aspects and our present finding that

dppe stabilizes cationic η^3-propargyl species more efficiently, we propose an alternative catalytic cycle involving cationic η^3-propargylpalladium complexes (Scheme 5).[15]

Scheme 5



1-5 Conclusion

I described the synthesis and characterization of cationic η^3-propargylpalladium complexes, which might be the more reactive intermediate in the catalytic reactions. Palladium prefers the η^3-propargyl coordination fashion more than platinum. In addition, the equilibrium mixture of cationic η^3-propargyl and neutral η^1-allenylpalladium complexes was observed . The equilibrium lies increasingly in favor of the cationic η^3-propargyl complex as the alkyl substituent is introduced at the propargylic position, the liberating ligand is Cl^-, and the bidentate ligand (dppe) is used in a polar solvent.

1-6 Experimental Section

General Procedures.

Most of commercially available reagents were used without further purification. All reactions and manipulations of air- and moisture-sensitive compounds were carried out under an atmosphere of dry Ar by use of standard vacuum line techniques. Melting points were determined on a Yanagimoto 1493 micro melting-point apparatus. NMR spectra were obtained on JEOL GSX-270, JEOL GSX-400, JEOL JNM-LA400, and Bruker AM 600 spectrometers. Chemical shifts are given in ppm using TMS or H_3PO_4 as a standard. High-resolution mass spectrum was taken with a JEOL JMS-700 mass spectrometer. Single crystal X-ray structure determinations were carried out on a Rigaku AFC5R diffractometer. Elemental analyses were obtained at the Analytical Center, Faculty of Engineering, Osaka University.

All of the solvents were distilled prior to use. Most commercially available reagents were used without further purification. *trans*-Pd(η^1-$CH_2C{\equiv}CSiMe_3$)(Cl)(PPh_3)$_2$ (**1a**),[5b] *cis*- and *trans*-Pt(η^1-$CH_2C{\equiv}CPh$)(Cl)(PPh_3)$_2$,[13a] ^{t}BuC≡CCH$_2$OH, ^{t}BuC≡CCH(Me)OH,[16] $Pd(PPh_3)_4$,[17] and $Pd_2(dba)_3{\cdot}CHCl_3$[18] were prepared according to the published methods. Chlorination and/or bromination of RC≡CCH(R')OH (R = Ph, R' = H; R = ^{t}Bu, R' = Me; R = ^{t}Bu, R' = H) was carried out according to a literature procedure.[19]

Preparation of a mixture of *trans*-Pd(η^1-$CH_2C{\equiv}CPh$)(Cl)(PPh_3)$_2$ and *trans*-Pd(η^1-C(Ph)=C=CH$_2$)(Cl)(PPh_3)$_2$ (1b).

In an adaptation of the literature procedure,[5b] to a suspension of 2.82 g (2.44 mmol) of $Pd(PPh_3)_4$ in 120 mL of THF was added 523.8 mg (3.48 mmol) of PhC≡CCH$_2$Cl at 25 °C under an argon atmosphere. The color of the mixture changed to yellow within 10 min, and after 40 min, the volume of the solvent was reduced to half by a rotary evaporator. After the addition of 600 mL of pentane, the yellow obtained precipitate was collected on a glass filter, and washed with 50 mL of diethyl ether and 60 mL of pentane. The yellow mixture of propargyl and allenyl complexes was dried under vacuum (1.17 g, 62%). Mp

136-140 °C (dec); Propargyl type: ^{1}H NMR ($CDCl_3$) δ 1.54 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 6.76 (s, CH_2C), 86.13 (s, CH_2C), 94.38 (s, $CCPh$); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 27.33 (s); Allenyl type: ^{1}H NMR ($CDCl_3$) δ 3.53 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 68.08 (s, CCH_2), 103.20 (t, J_{PC} = 2.9 Hz, CCH_2), 199.60 (t, J_{PC} = 4.1 Hz, PhCC); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 23.89 (s); Anal. Calcd for $C_{45}H_{37}ClP_2Pd$: C, 69.15; H, 4.77%. Found: C, 69.05; H, 5.01%.

Preparation of cationic [Pd(η^3-$Me_3SiCCCH_2$)(PPh_3)$_2$][BF_4] (2a).

To a solution of 50.7 mg (0.0652 mmol) of **1a** in 2.5 mL of CH_2Cl_2 was added 16.0 mg (0.0822 mmol) of $AgBF_4$ at 25 °C under an argon atmosphere and the suspension was stirred for 15 min. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure in a rotary evaporator. Then, the red solids were washed with four portions of 10 mL of hexane, and reprecipitation from CH_2Cl_2/hexane gave white-yellow solids of **2a** (47.4 mg, 88%). Mp 108-109 °C (dec); ^{1}H NMR ($CDCl_3$) δ -0.29 (s, 9H), 3.07 (dd, J_{PH} = 7.8, 1.9 Hz, 2H), 7.15-7.50 (m, 30H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 0.26 (s, $Si(CH_3)_3$), 52.40 (dd, J_{PC} = 39.1, 6.2 Hz, CCH_2), 104.74 (d, J_{PC} = 40.4 Hz, $SiCC$), 113.84 (dd, J_{PC} = 8.1, 8.1 Hz, CCH_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ29.90 (d, J_{PP} = 46.4 Hz), 30.68 (d, J_{PP} = 46.4Hz); Anal. Calcd for $C_{42}H_{41}P_2PdSiBF_4$: C, 60.84; H, 4.98%. Found: C, 60.82; H, 5.13%.

Preparation of cationic [Pd(η^3-$PhCCCH_2$)(PPh_3)$_2$][BF_4] (2b).

The procedure was similar to that for **2a**. Yield 94%; Mp 99-100 °C (dec); ^{1}H NMR ($CDCl_3$) δ 3.26 (dd, J_{PH} = 7.6, 2.0 Hz, 2H), 6.68-6.82 (m, 4H), 6.97-6.20 (m, 12H), 6.29-7.51 (m, 19H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 51.61 (dd, J_{PC} = 35.9, 5.9 Hz, CCH_2), 94.57 (dd, J_{PC} = 7.3, 7.3 Hz, CCH_2), 105.58 (dd, J_{PC} = 41.4, 4.9 Hz, PhCC); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 30.16 (d, J_{PP} = 47.7 Hz), 30.85 (d, J_{PP} = 47.7 Hz); Anal. Calcd for $C_{45}H_{37}P_2PdBF_4\cdot(H_2O)$: C, 63.51; H, 4.62%. Found: C, 63.80; H, 4.54%.

Mesylation of ^{t}BuC≡CCH(Me)OH.

In an adaptation of a literature procedure,[20] to a solution of 3.79 g (30.0 mmol) of ^{t}BuC≡CCH(Me)OH in 100 mL of CH_2Cl_2 was added 6.27 mL of NEt_3 at -60 °C under an argon atmosphere. After 50 min, to the solution was added 3.10 mL (40.1 mmol) of CH_3SO_2Cl, and the mixture was stirred for 10 min. The reaction mixture was gradually warmed to 25 °C, and then poured into 200 mL of H_2O. The resulting mixture was extracted with CH_2Cl_2 and the organic layer was dried over $MgSO_4$ and concentrated. The concentrate was distilled (77 °C/0.5 mmHg) to give 5.51 g (90 %) of **^{t}BuC≡CCH(Me)OSO$_2$Me(3)**. ^{1}H NMR ($CDCl_3$) δ 1.23 (s, 9H), 1.61 (d, J = 6.6 Hz, 3H), 3.12 (s, 3H), 5.28 (q, J = 6.6 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 22.94, 27.40, 30.53, 39.07, 69.16, 75.41, 97.28; HRMS Calcd for $C_8H_{13}O_3S$: [M^+ - CH_3], 189.0585. Found: *m/z* 189.0591.

Preparation of cationic [Pd(η^3-^{t}BuCCCH(Me))(dppe)][OTf] (4).

To a CH_2Cl_2 solution (5.0 mL) of 150 mg (0.145 mmol) of $Pd_2(dba)_3{\cdot}CHCl_3$ and 116 mg (0.290 mmol) of dppe was added 65.1 mg (0.319 mmol) of **3** under an argon atmosphere. After 15 min, to the reaction mixture was added 150 mg (0.869 mmol) of NaOTf (OTf = trifluoromethanesulfonate), and the suspension was stirred for 20 min. The reaction mixture was concentrated in vacuo, and the orange residue was dissolved in CH_2Cl_2. After filtration, the filtrate was concentrated in vacuo again, and the residue was washed with seven portions of 10 mL of ether. Recrystallization from CH_2Cl_2/ether/hexane gave yellow crystals of **4** (192 mg, 87%). Mp 80-82 °C (dec); ^{1}H NMR ($CDCl_3$) δ 0.97 (s, 9H), 1.07 (td, J_{PH} = 8.8 Hz, J_{HH} = 6.8 Hz, 3H), 2.26-2.55 (m, 2H), 2.55-2.94 (m, 2H), 4.30 (dq, J_{PH} = 7.1 Hz, J_{HH} = 6.8 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 17.08 (d, J_{PC} = 4.4 Hz, CH_3), 27.90 (dd, J_{PC} = 33.2, 13.5 Hz, PCH_2CH_2P), 30.15 (dd, J_{PC} = 33.9, 14.7 Hz, PCH_2CH_2P), 31.82 (s, C(CH_3)$_3$), 32.13 (s, C(CH$_3$)$_3$), 66.19 (dt, J_{PC} = 37.6, 6.5 Hz, CCH), 96.83 (d, J_{FC} = 6.3 Hz, CCH), 120.08 (d, J_{PC} = 34.6 Hz, CCCH), 120.87 (q, J_{FC} = 321.3 Hz, CF_3); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 54.90 (d, J_{PP} = 42.8 Hz), 56.00 (d, J_{PP} = 42.8 Hz); Anal. Calcd for $C_{35}H_{37}F_3O_3P_2SPd{\cdot}(CH_2Cl_2)$: C, 50.99; H, 4.64%. Found: C, 51.25; H, 4.70%.

In situ reaction of Pd(η^1-$CH_2C{\equiv}CSiMe_3$)(Cl)(PPh_3)$_2$ (1a) with $NaBPh_4$.

A mixture of 19.5 mg (0.0251 mmol) of **1a** and 8.6 mg (0.0251 mmol) of $NaBPh_4$ was dissolved in 0.4 mL of $CDCl_3$ and 0.2 mL of $(CD_3)_2CO$ under an argon atmosphere. The reaction was monitored by ^1H NMR. Cationic **[Pd(η^3-$Me_3SiCCCH_2$)-(PPh_3)$_2$][BPh_4]** (**5a**) was obtained after 5 min (100%), which gradually decomposed to afford **$Me_3SiC{\equiv}CCH_2Ph$** (30%) and **$Me_3Si(Ph)C{=}C{=}CH_2$** (3%) in the solution after 4 h. ^1H NMR spectrum of **5a** ($CDCl_3$) δ 2.99 (d, J_{PH} = 7.8 Hz, 2H). Registry No. $Me_3SiC{\equiv}CCH_2Ph$, 31683-47-3; $Me_3Si(Ph)C{=}C{=}CH_2$, 71321-00-1.

In situ reaction of a mixture of *trans*-Pd(η^1-$CH_2C{\equiv}CPh$)(Cl)(PPh_3)$_2$ and *trans*-Pd(η^1-$C(Ph){=}C{=}CH_2$)(Cl)(PPh_3)$_2$ (1b) with $NaBPh_4$.

The procedure was similar to that for **1a**. Cationic **[Pd(η^3-$PhCCCH_2$)-(PPh_3)$_2$][BPh_4]** (**5b**) was obtained after 5 min (100%). ^1H NMR spectrum of **5b** ($CDCl_3$) δ 3.15 (d, J_{PH} = 7.8 Hz, 2H).

In situ reaction of ^{t}BuC≡CCH(Me)Cl (6a) with 1/2$Pd_2(dba)_3{\cdot}CHCl_3$ and dppe.

To a $CDCl_3$ solution (0.6 mL) of **6a** (2.4 mg, 0.017 mmol) in an NMR tube were added 11.2 mg (0.0108 mmol) of $Pd_2(dba)_3{\cdot}CHCl_3$ and 8.6 mg (0.022 mmol) of dppe under an atmosphere of argon. The reaction was monitored by ^1H NMR. Cationic **[Pd(η^3-^{t}BuCCCH(Me))(dppe)][Cl]** (**7a**) (45%) and ***cis*-Pd(η^1-$C(Bu^t){=}C{=}CH(Me)$)(Cl)(dppe)** (**8a**) (15%) were obtained after 30 min. ^1H NMR spectrum of **7a** ($CDCl_3$) δ 0.96 (s, 9H), 1.07 (td, J_{PH} = 8.5 Hz, J_{HH} = 6.8 Hz, 3H), 4.25 (tq, J_{PH} = 4.4 Hz, J_{HH} = 6.8 Hz, 1H), ^1H NMR spectrum of **8a** ($CDCl_3$) δ 0.57 (dd, J_{PH} = 8.9 Hz, J_{HH} = 6.8 Hz, 3H), 1.55 (s, 9H), 3.01 (q, J_{HH} = 6.8 Hz, 1H). The same reaction was carried out in DMF-d_7 (**7a**, 65%; **8a**, 8%) and C_6D_6 (**7a**, 7%).

In situ reaction of ^{t}BuC≡CCH(Me)Br (6b) with 1/2Pd$_2$(dba)$_3$·CHCl$_3$ and dppe.

The procedure was similar to that of **6a**. Cationic **[Pd(η^3-^{t}BuCCCH(Me))-(dppe)][Br]** (**7 b**) (49%) and ***cis*-Pd(η^1-C(Bu^t)=C=CH(Me))(Br)(dppe)** (**8b**) (23%; major/minor = 9/5) were obtained after 30 min. ^{1}H NMR for **7b** ($CDCl_3$) δ 0.94 (s, 9H), 1.05 (td, J_{PH} = 8.5 Hz, J_{HH} = 6.8 Hz, 3H), 4.24 (tq, J_{PH} = 4.3 Hz, J_{HH} = 6.8 Hz, 1H), ^{1}H NMR for **8b**-major ($CDCl_3$) δ 0.59 (dd, J_{PH} = 9.3 Hz, J_{HH} = 6.6 Hz, 3H), 1.54 (s, 9H), 3.11 (q, J_{HH} = 6.6 Hz, 1H), ^{1}H NMR for **8b**-minor ($CDCl_3$) δ 0.55 (dd, J_{PH} = 9.0 Hz, J_{HH} = 6.3 Hz, 3H), 1.52 (s, 9H), 2.99 (q, J_{HH} = 6.3 Hz, 1H).

Reaction of ^{t}BuC≡CCH(Me)Cl (6a) with Pd(PPh$_3$)$_4$.

To a $CDCl_3$ solution (0.6 mL) of **6a** (2.3 mg, 0.016 mmol) was added 16.6 mg (0.0144 mmol) of Pd(PPh_3)$_4$ under an atmosphere of argon. The reaction was monitored by ^{1}H NMR. ***trans*-Pd(η^1-C(^{t}Bu)=C=CH(Me))(Cl)(PPh$_3$)$_2$** (**9**) was obtained after 30 min (94%). ^{1}H NMR ($CDCl_3$) δ 0.57 (d, J_{HH} = 6.6 Hz, 3H), 1.54 (s, 9H), 3.08 (q, J_{HH} = 6.6 Hz, 1H). The same reaction was carried out in DMF-d_7 (69%).

In situ reaction of ^{t}BuC≡CCH$_2$Cl (6c) with 1/2Pd$_2$(dba)$_3$·CHCl$_3$ and dppe.

The procedure was similar to that of **6a**. ***cis*-Pd(η^1-CH$_2$C≡C^{t}Bu)(Cl)(dppe)** (**10**) was obtained after 30 min (76%). ^{1}H NMR ($CDCl_3$) δ 1.02 (s, 9H), 1.26 (s, 2H). The same reaction was carried out in DMF-d_7 (79%).

Single crystal X-ray diffraction study.

All data were obtained on a Rigaku AFC-5R diffractometer with graphite-monochromated Mo-Kα radiation. All calculations were carried out with the TEXSAN crystallographic software package of Molecular Structure Corporation. The structure was solved by the direct method and refined by the full-matrix least-squares procedure, the function minimized being $\Sigma w(|F_o|-|F_c|)^2$. The non-hydrogen atoms were refined anisotropically. All the positions of the hydrogen atoms were calculated by

stereochemical considerations.

[Pd(η^3-$Me_3SiCCCH_2$)(PPh_3)$_2$][BF_4] (2a).

A yellow crystal (0.20 × 0.20 × 0.50 mm) was obtained from CH_2Cl_2/hexane at -30 °C and was mounted on a glass fiber with epoxy resin. $C_{45}H_{37}BF_4P_2Pd$, M = 832.94, triclinic, space group $P\bar{1}$*(#2)*, a = 12.034(1) Å, b = 16.139(2) Å, c = 10.555(2) Å, α = 105.49(1)°, β = 92.30(1)°, γ = 101.60(1)°, V = 1925.6(5) Å^3, Z = 2, D_{calc} = 1.436 g/cm^3, F(*000*) = 848.00, μ(Mo-Kα) = 6.16 cm^{-1} by least squares refinement on diffractometer angles from automatically centered reflections, 2θ range 23.0-25.7°, λ = 0.71069 Å. The final R and R_w values were 0.080 and 0.107, respectively, for 3932 reflections (I > 3.00σ(I)).

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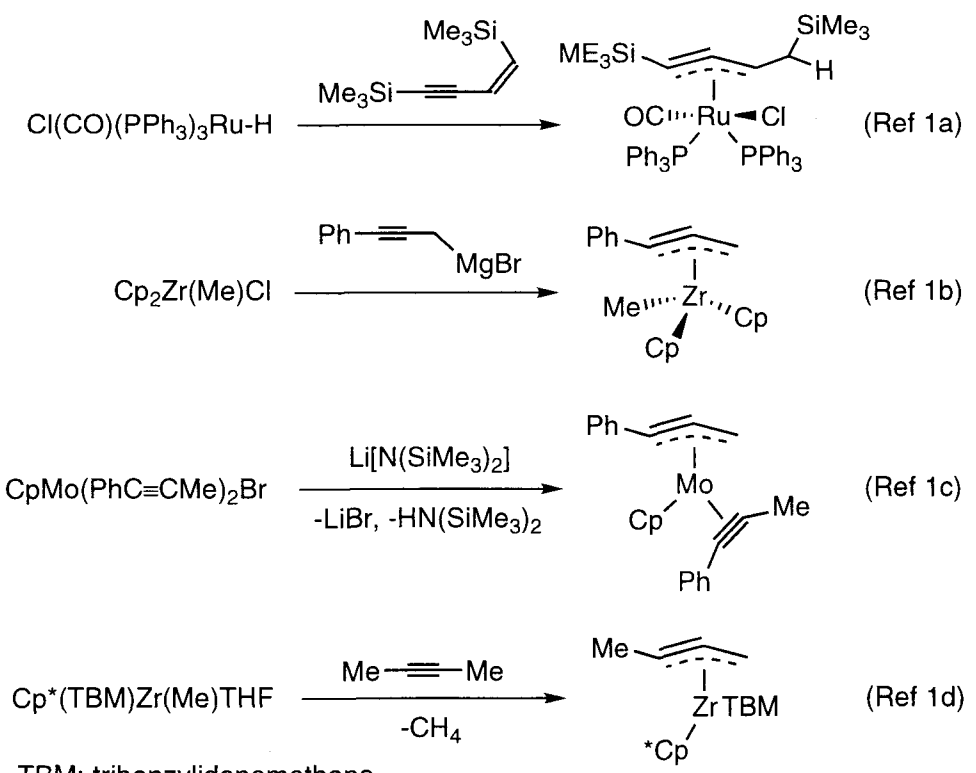
Chapter 2

Neutral η^3-allenyl/propargylpalladium monomer and η^1-propargylpalladium halide dimer

2-1 Introduction

Compared to the considerable progress in the cationic type η^3-allenyl/propargyl mononuclear transition-metal complexes (see Chapter 1), much less has still been elucidated on the bonding, structure, and reactivity of the neutral type η^3-propargyl ones. Since 1991, some stable neutral η^3-propargyl complexes have been prepared by various synthetic routes (Scheme 1), including 1,4-addition of metal-hydride to the conjugated enyne,[1a] reaction of metal halides with propargyl nucleophiles,[1b] dehydrohalogenation reaction and rearrangement of halogenobis(alkyne) complex,[1c] and σ-bond metathesis reaction.[1d]

Scheme 1



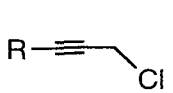
TBM: tribenzylidenemethane
Cp*: C_5Me_5

Exploration of new chemistry of η^3-propargylpalladium complexes appears of potentially synthetic and theoretical significance[2] in view of the major role played by η^3-allylpalladiums in organic synthesis.[3] Mononuclear cationic η^3-propargylpalladium(II) and platinum(II) species are very prone to undergo nucleophilic attack at the central carbon of the propargyl group to afford a metallacyclobutene framework (see Chapter 1), while dinuclear neutral η^3-propargylpalladium(I) complexes are susceptible to attack of an electrophile at central carbon, yielding μ-vinylcarbene dipalladium complexes (see Chapter 3).

In this chapter, I wish to report the first synthesis and stability and reactivity aspects of neutral η^3-propargylpalladium complexes from which fundamental insights were newly gained into the nature of bonding in and the potential role in synthetic application of η^3-allenyl/propargyl transition-metal complexes.

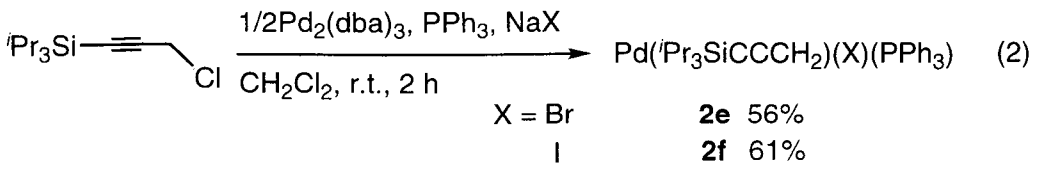
2-2 Synthesis and characterization of neutral η^3-allenyl/propargylpalladium monomer and η^1-propargylpalladium halide dimer

The reaction of propargyl chlorides (**1a-d**) with $Pd_2(dba)_3{\cdot}CHCl_3$ and PPh_3 (Pd/PPh_3 = 1/1) in CH_2Cl_2 at room temperature afforded new complexes $Pd(RCCCH_2)(Cl)(PPh_3)$ (**2a-d**) (eq. 1). Further, the analogous reaction of **1d** in the presence of NaX (X = Br, I) gave the corresponding bromide and iodide $Pd(^iPr_3SiCCCH_2)(X)(PPh_3)$ (**2e**: X = Br; **2f**: X = I) (eq. 2).



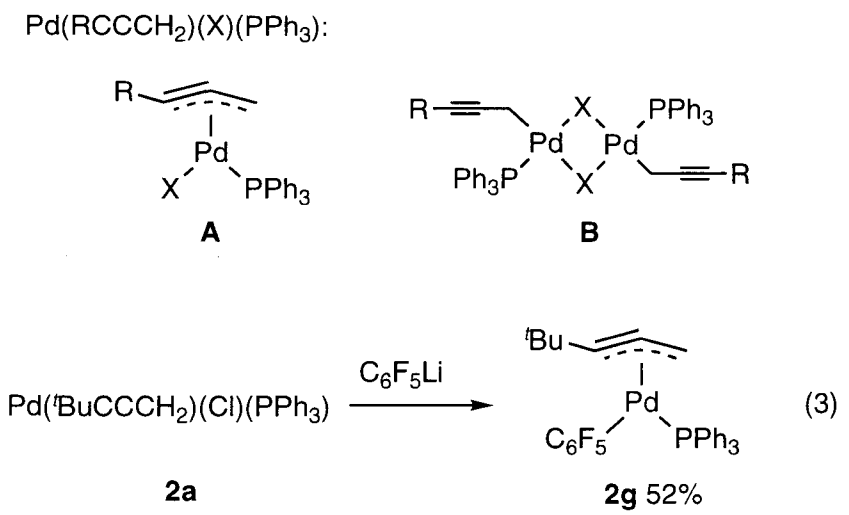
$$\xrightarrow[CH_2Cl_2,\ r.t.,\ 2\ h]{1/2Pd_2(dba)_3,\ PPh_3} Pd(RCCCH_2)(Cl)(PPh_3) \qquad (1)$$

1a: R = ^{t}Bu	**2a** 84%
1b: R = $(CH_3)_3Si$	**2b** 84%
1c: R = ^{t}Bu$(CH_3)_2Si$	**2c** 46%
1d: R = ^{i}Pr$_3$Si	**2d** 84%



These complexes exist as a mixture of the η^3-allenyl/propargyl monomer (**A**) and the halide-bridged η^1-propargyl dimer (**B**) in solution (Scheme 2, see below). The dimeric structure of **2d** in the solid state was confirmed by X-ray crystallographic study (see Chapter 2-3 Figure 1). The treatment of **2a** with C_6F_5Li gave Pd(^{t}BuCCCH$_2$)-(C_6F_5)(PPh_3) (**2g**) (eq. 3), which exists in the monomeric η^3-propargyl structure both in the solid state (analyzed by X-ray crystallographic study, see Chapter 2-3 Figure 2) and in a solution (Vapor Pressure Osmometry (VPO) molecular weight in chloroform at 35 °C; found, 638 at 1.08×10^{-2} M; calcd for monomer, 631).

Scheme 2



Both η^3-type monomer and η^1-type dimer are confirmed by ^{1}H-NMR spectra on **2c-e** in chloroform-*d* at room temperature. As to **2a**, **b**, **f**, however, the η^3-type monomer is observed by NMR spectra to dominate under the same condition. In addition, the molecular weight of **2a** in chloroform measured by vapor pressure osmometry agreed closely with the monomer (VPO molecular weights in chloroform at 35 °C; found, 500 at

1.02×10^{-2} M; calcd for monomer, 499). The ^{13}C NMR chemical shift of the methylene carbon of the $CCCH_2$ unit of **2a** at δ 36.70 is not in agreement with those reported for η^1-propargyl and η^1-allenyl complexes[4] but is consistent with the η^3-coordination mode. The large carbon-phosphorus coupling (J_{PC} = 40.0 Hz) for the carbon attached to *tert*-butyl group indicates that PPh_3 is located *trans* to this carbon as depicted in Scheme 2. The VPO molecular weights of **2d** in chloroform at 35 °C were found as 643 and 717 at concentrations 3.67×10^{-3} and 1.20×10^{-2} M (calcd for monomer, 600 and dimer, 1199). Moreover, ^1H and ^{13}C NMR spectra of **2d** ($CDCl_3$) at room temperature showed two separate sets of resonances, with the relative ratio dependent on the concentration. One ^{13}C set which increased with the increasing concentration exhibited the higher magnetic field shift for CH_2 carbon (δ 8.10 ppm, s) and the lower magnetic field shift for RC≡ carbon (δ 112.70 ppm, s) than those of the other set (δ 35.64 ppm, s; δ 105.17 ppm, d, J_{CP} = 35.3 Hz) which were analogous, in shifts or ^{31}P coupling patterns, to those of the η^3-propargyl ligand in **2g** (δ 43.80 ppm, s; 114.25 ppm, d, J_{CP} = 55.2 Hz). Moreover, the chemical shifts in the former set were quite close to those in *trans*-Pd(η^1-$CH_2C{\equiv}CSiPr^i_3$)-(Cl)$(PPh_3)_2$.[5] These results indicate that **2d** in chloroform exists as an equilibrium mixture of the η^3-allenyl/propargyl monomer (**A**) and η^1-propargyl dimer (**B**) (see Chapter 2-4). ^1H and ^{13}C NMR spectra in $CDCl_3$ at room temperature also showed two separate sets of resonances for **2c** and **2e**, but only one set for **2a**, **2b**, and **2f**, with the chemical shifts of the latter corresponding to the η^3-coordination mode (**A**), which was also supported by the VPO molecular weights.[6]

2-3 X-ray structure of neutral η^3-allenyl/propargylpalladium monomer and η^1-propargylpalladium chloride dimer

The molecular structure of a crystal obtained from a dichloromethane-hexane solution of **2d** was analyzed by X-ray diffraction technique (Figure 1). The result indicates that the crystal contains the η^1-propargylpalladium chloride dimer structure, although both η^3-type monomer and η^1-type dimer exist in chloroform-*d*. The C1-C2 and C2-C3 bond lengths are 1.200(6) Å and 1.437(5) Å respectively. C3 and C3*, Pd and Pd*, P and P* and two chlorines are located almost on the same plane. This is the first X-ray structural information of η^1-propargyl transition-metal complexes.

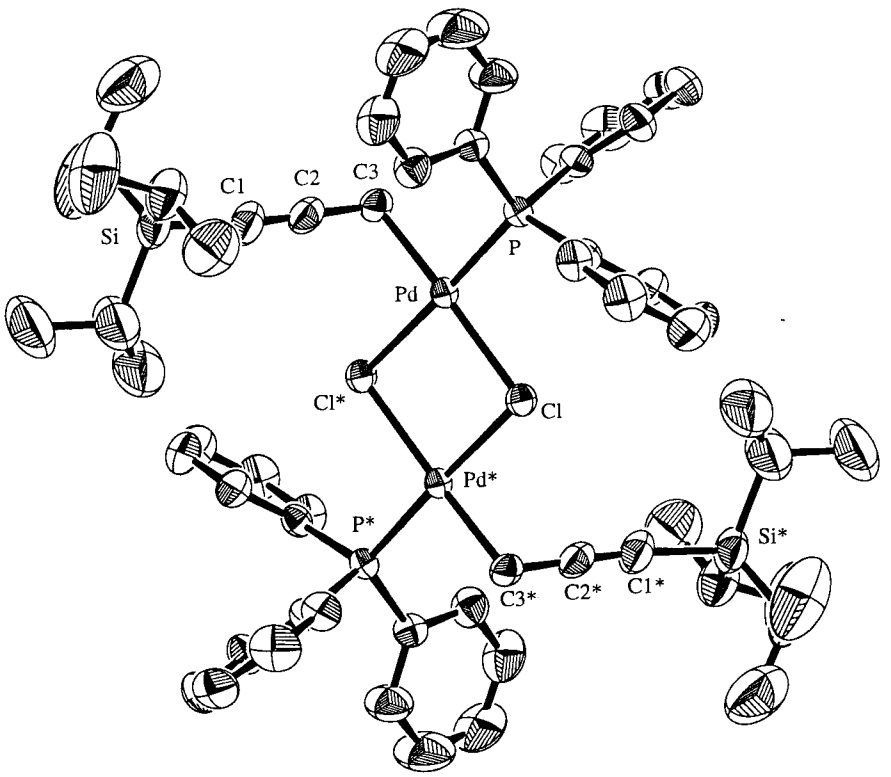


Figure 1. Molecular structure of **2d**(η^1-type dimer). Selected bond distances (Å): Pd-Cl = 2.441(5), Pd-Cl* = 2.408(1), Pd-P = 2.225(1), Pd-C3 = 2.070(3), C1-C2 = 1.200(6), C2-C3 = 1.437(5). Selected angle (deg): C2-C3-Pd = 108.0(2), C3-Pd-Cl* = 90.0(1).

On the other hand, as to X-ray structure of **2g** the Pd-CH_2 bond (2.156(7) Å) is considerably longer than that in **2d** (2.070(3) Å), possibly reflecting both intrinsic difference of bond strength between η^1- and η^3-coordination[7] and the stronger trans influence of C_6F_5 than Cl.[8] The geometry of η^3-propargyl ligand in **2g** is similar to that of [Pd(η^3-PhCCCH_2)(PPh_3)$_2$][BF_4] (see Chapter 1-3); Pd, P, C4 and η^3-propargyl carbons are located almost on the same plane (dihedral angle between Pd-P-C4 and C1-C2-C3 = 3.93°).

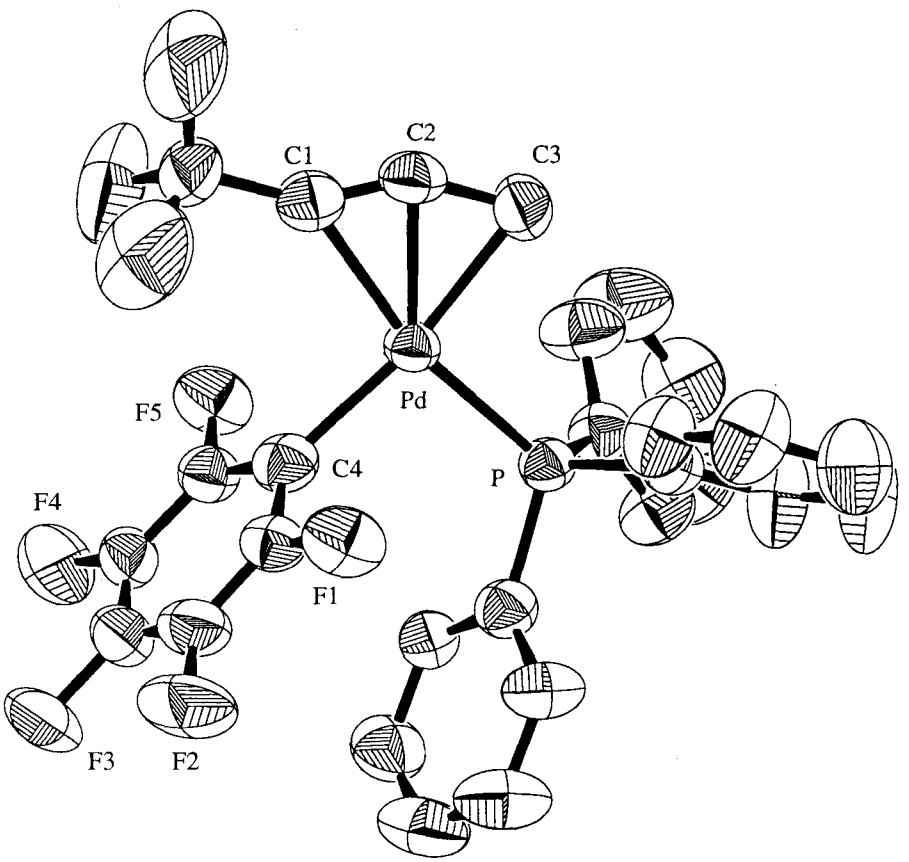
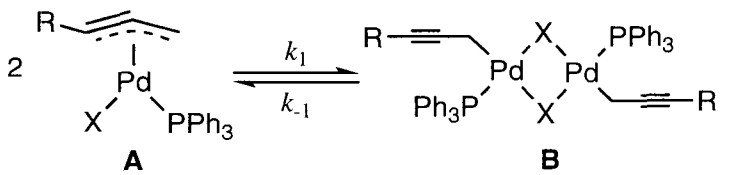


Figure 2. Molecular structure of **2g** (η^3-type monomer). Selected bond distances (Å): Pd-C1 = 2.238(7), Pd-C2 = 2.116(6), Pd-C3 = 2.156(7), C1-C2 = 1.244(9), C2-C3 = 1.38(1). Selected angle (deg): C1-C2-C3 = 151.6(7). Dihedral angles (deg): Pd-P-C4, C1-C2-C3 = 3.93.

2-4 Equilibrium between η^3-allenyl/propargylpalladium monomer and η^1-propargylpalladium halide dimer

The equilibrium constants between η^3- and η^1-propargyl isomers were determined by ^{1}H NMR spectra in $CDCl_3$ and C_6D_6 at 25 °C (Table 1).



A **B**

$K_1 = k_1/k_{-1}$

Table 1 Equilibrium constant K_1 (M^{-1}).

No.	R	X	In $CDCl_3$	In C_6D_6
2a	^{t}Bu	Cl	<< 1	<< 1
2b	Me_3Si	Cl	<< 1	14
2c	^{t}Bu$(Me)_2Si$	Cl	2.4	30
2d	^{i}Pr$_3$Si	Cl	16	450
2e	^{i}Pr$_3$Si	Br	5.2	45
2f	^{i}Pr$_3$Si	I	<< 1	21

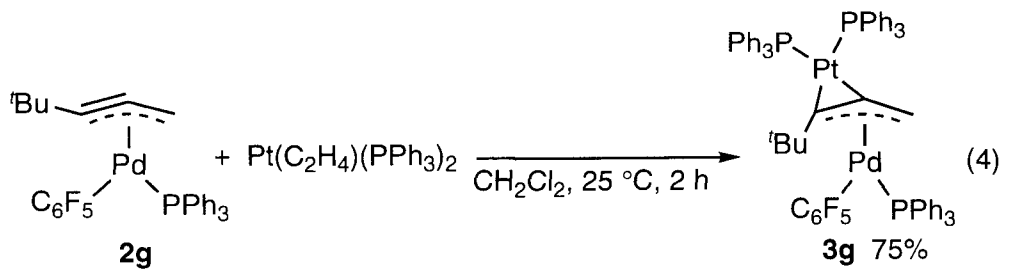
[a] K_1 calculated by integrations of ^{1}H NMR signals of A and B at 25 °C.

These data show that the η^3-propargyl form is favored by the less bulky substituent R and more polar solvent. It is quite remarkable that the equilibrium lies increasingly in favor of the η^3-type monomer as chloride is replaced by bromide, and bromide by iodide (**2d**, **2e**, **2f**). Generally, the ability of the halide ligand to act as a bridging ligand increases with increasing atomic number;[9] this tendency was estimated by the degree of bridge splitting by a hard ligand such as amine. On the other hand, the conversion from B to A involves bridge splitting by the C≡C ligand upon which a considerable change of the electronic structure at palladium atom would be induced. It is probable that the symbiotic effect[10] of the softer halide ligand is at work. In other words, the η^3-propargyl coordination may require the softer nature of the palladium center than the η^1-coordination, and this requirement would be better fulfilled by the iodide. Another result of

significance is the thermodynamic parameters for the equilibrium of **2a** in toluene-d_8 (25 °C to -80 °C), ΔH^0 = -9.0 kJ mol^{-1} and ΔS^0 = -33 J mol^{-1}K^{-1} which indicate that the η^3-type monomer is favored at 25 °C not by the enthalpy but by the entropy term.

2-5 The reactivity of neutral η^3-allenyl/propargylpalladium complexes

I have investigated reactivities of **2** with some nucleophiles. Although **2** did not react with MeOH and Et_2NH which added to the C≡C bond of cationic η^3-allenyl/propargyl complexes of Pd and Pt,[11a,b,c] **2g** did react with a Pt(0) nucleophile in a formally analogous manner. Thus, addition of 1 equiv $Pt(C_2H_4)(PPh_3)_2$ to **2g** in CH_2Cl_2 for 2 h at 25 °C afforded new complex **3g** (75%) (eq. 4) of which X-ray crystallographic analysis revealed a remarkable structure containing μ-η^2:η^3-^{t}BuCCCH$_2$ ligand (Figure 3).



(4)

The C1-C2 bond is longer (1.335(7) Å) and the C1-C2-C3 angle smaller (135.5(6)°) than those of **2g**, and the η^3-ligand is no longer co-planar with the Pd-P1-C4 plane (dihedral angle between Pd-P1-C4 and C1-C2-C3 = 49.16°). In contrast to other dimetal complexes containing μ-η^2:η^3-RCCCH$_2$ ligands[12] **3g** does not possess a metal-metal bond (Pd-Pt = 3.33 Å). This fact, together with the great ease of its formation, makes the present complex quite a unique member of the complexes containing the similar kind of ligands.

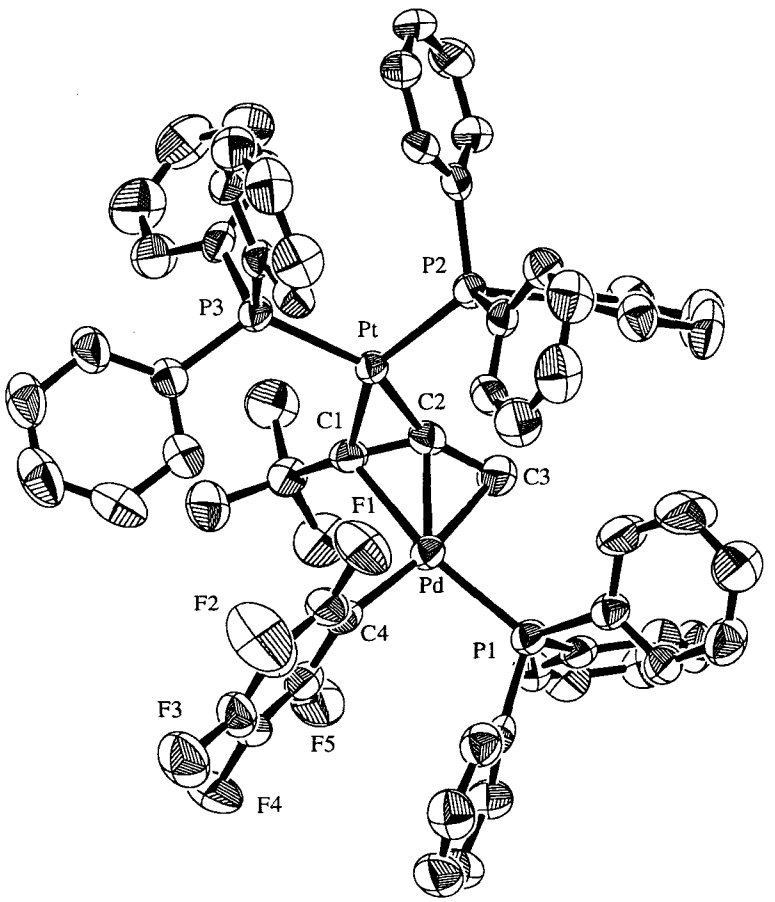
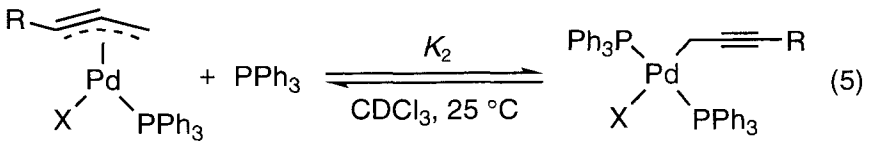


Figure 3. Molecular structure of **3g**. Selected bond distances (Å): Pd-C1 = 2.304(6), Pd-C2 = 2.153(6), Pd-C3 = 2.142(6), Pt-C1 = 2.063(6), Pt-C2 = 2.022(6), C1-C2 = 1.335(7), C2-C3 = 1.391(7). Selected angle (deg): C1-C2-C3 = 135.5(6). Dihedral angle (deg): Pd-P1-C4, C1-C2-C3 = 49.16.

The addition of equimolar PPh_3 to **2a-f** in $CDCl_3$ generated η^1-propargylpalladium complexes almost quantitatively (eq. 5, K_2 >100 M^{-1}),[13] while both η^3- and η^1-propargyl complexes lie in equilibrium in the case of **2g** (K_2 = 25 M^{-1}), showing that the aryl is a better ligand than the halides to stabilize η^3-allenyl/propargyl coordination. In case of the analogous allylpalladium complex, η^3-bonding structure is much more stable than η^1-bonding one.[14] The order of the auxiliary ligand to stabilize the η^3-propargyl coordination (C (C_6F_5) > I > Br > Cl) found here is the same as the order (X = C (PhC≡C)

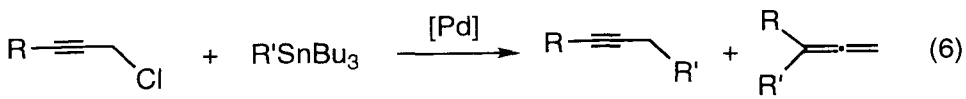
> I > Br > Cl) of the rate of the isomerization of Pt(η^1-$CH_2C{\equiv}CPh$)(X)(PPh_3)$_2$ to the allenyl isomer via the five-coordinate η^3-propargyl intermediate.[15]



(5)

2-6 Cross coupling reactions proceeding through η^1- and η^3-allenyl/propargyl-palladium intermediates

I have examined the effect of PPh_3/Pd ratio in the catalyst precursor on the efficiency of Migita-Stille coupling between $RC{\equiv}CCH_2Cl$ and $R'SnBu_3$ (eq. 6).



(6)

R = ^{t}Bu, Me_3Si; R' = Ph, $PhC{\equiv}C$

As shown in Table 2, the coupling using $PhSnBu_3$ proceeded much more rapidly and cleanly by means of a catalyst precursor, $1/2Pd_2(dba)_3$ + PPh_3 than $Pd(PPh_3)_4$. The regioselectivity of the coupling (at propargylic or vinyl carbon) was highly irrespective of the PPh_3/Pd ratio, with the propargyl product predominating. For the reaction of $PhC{\equiv}CSnBu_3$ where the allenyl product dominated, the effect of the PPh_3/Pd ratio on the reaction efficiency was not so easily recognizable. Even with the use of PPh_3/Pd = 4/1 catalyst, $PhC{\equiv}CSnBu_3$ reacted sufficiently fast in contrast to the very slow reaction of $PhSnBu_3$ carried out by means of the same catalyst system.

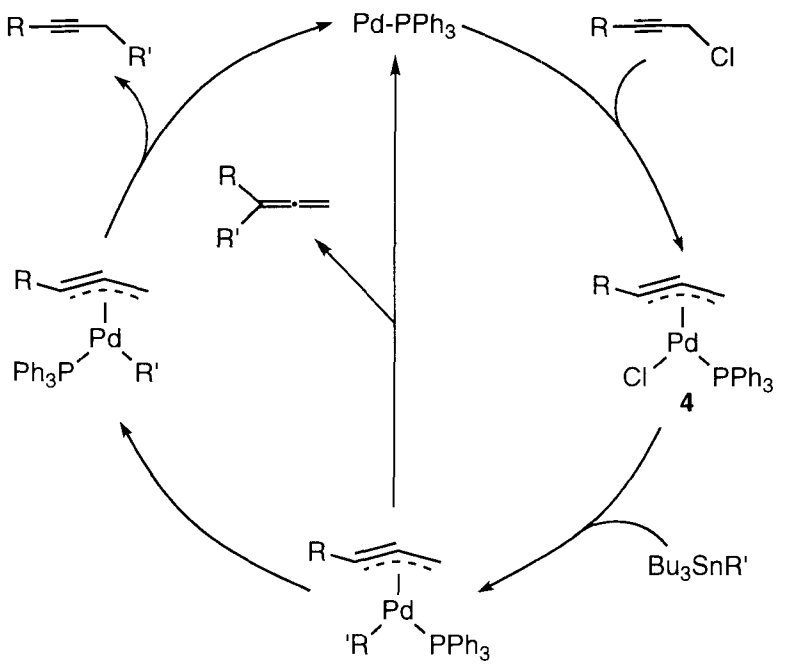
Table 2 Results of cross-coupling, eq. 6[a]

[Pd][b]	R	R'	Time (h)	yield (%)	Ratio (yne/allene)
4L/Pd	^{t}Bu	Ph	54	26	99/1
L/Pd	^{t}Bu	Ph	4	95	96/4
4L/Pd	$SiMe_3$	Ph	80	30	98/2
L/Pd	$SiMe_3$	Ph	13.5	83	96/4
4L/Pd	^{t}Bu	C≡CPh	2	100	3/97
L/Pd	^{t}Bu	C≡CPh	3	73	4/96

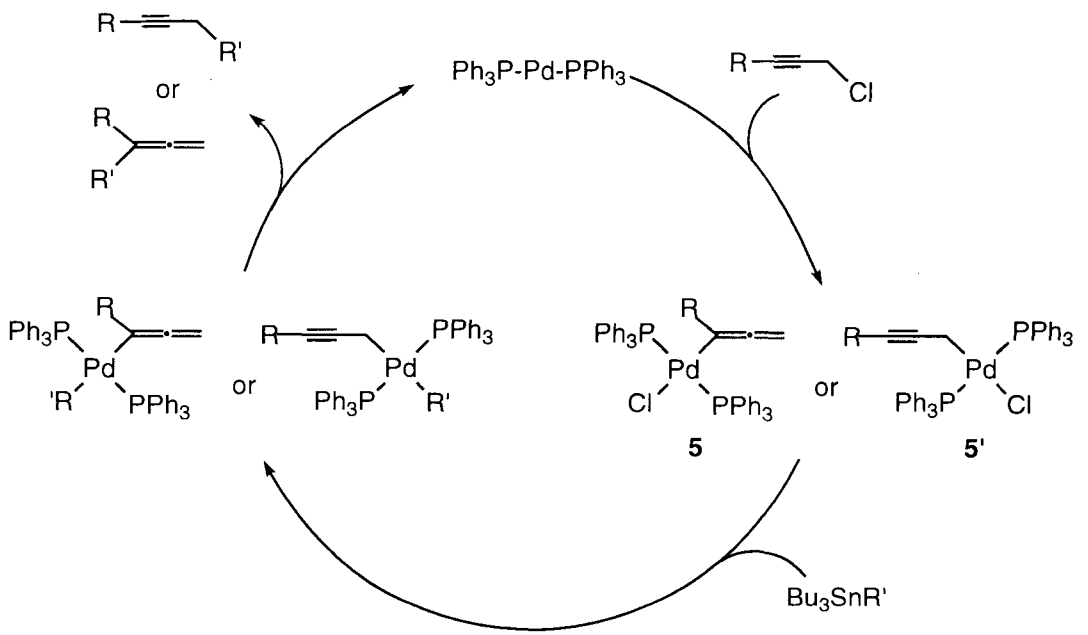
[a] Condition: [$RC{\equiv}CCH_2Cl$] 0.50 mmol; [$R'SnBu_3$] 0.55mmol; [Pd] 5 mol% in THF (1 ml) at 50 °C.
[b] 4L/Pd = $Pd(PPh_3)_4$; L/Pd = $1/2Pd_2(dba)_3$+PPh_3.

In order to explain the results shown above, we propose that the catalytic reaction with the PPh_3/Pd = 1/1 system involves intervention of η^3-propargylpalladium species, $Pd(\eta^3\text{-}RCCCH_2)(Cl)(PPh_3)$ (**4**, Scheme 3), whereas the reaction with PPh_3/Pd = 4/1 proceeds through conventional η^1-allenyl or propargyl species, $Pd(R'')(Cl)(PPh_3)_2$ (R'' = $\eta^1\text{-}CR{=}C{=}CH_2$ or $\eta^1\text{-}CH_2C{\equiv}CR$) (**5** or **5'** Scheme 4) for the reason explained below. We further propose that the rate-determining step of the overall catalysis is the reaction of intermediate **4** or **5**, and the rate of such transmetalation step depends on the PPh_3/Pd ratio in the organopalladium intermediate.

Scheme 3



Scheme 4



Oxidative addition of $RC{\equiv}CCH_2Cl$ with $1/2Pd_2(dba)_3$+PPh_3 afforded the product of composition $Pd(RCCCH_2)(Cl)(PPh_3)$, which exists in solution as a mixture of η^3-allenyl/propargyl monomer **A** and η^1-propargyl dimer **B** (Chapter 2-4). The equilibrium constant for monomer-dimer interconversion with R = ^{t}Bu ($K << 1\ M^{-1}$) suggests that, under the condition of catalysis (Pd total concentration being 5×10^{-3} - 5×10^{-2} M), the oxidative addition product $Pd(RCCCH_2)(Cl)(PPh_3)$ exists almost exclusively as the monomer **A**. According to eq. 5, addition of 1 equiv. PPh_3 to **4** results in complete conversion of **4** to intermediate **5/5'** in the catalyst system PPh_3/Pd = 4/1.

In order to look in more detail at the mechanism, we examined the kinetics of the cross-coupling between ^{t}BuC≡CCH_2Cl and $PhSnBu_3$ in 1/1 molar ratio catalyzed by the PPh_3/Pd = 1/1 system in THF at 50°C. I followed the decay of the chloride reagent by GLC and the result is shown in Figure 4. At a given concentration of Pd complex, the concentration of the chloride decreased in a first-order dependence. This indicates that, in view of the relation [^{t}BuC≡CCH_2Cl] = [$PhSnBu_3$] in the course of the catalysis, the rate (-d[^{t}BuC≡CCH_2Cl]/dt = -d[$PhSnBu_3$]/dt) is linearly dependent on only one reactant, the chloride or the tin compound. Since I confirmed that the tin participates in the rate-determining step (see below), I conclude that the rate is dependent on the tin concentration

in first-order fashion. The pseudo first-order rate constants determined from this relation were linearly dependent on the catalyst concentration. Thus, the rate was first-order in both the concentration of the tin reagent and total Pd concentration (eq. 7). The second-order rate constant, k_2 was obtained as 3.8×10^{-3} M^{-1} s^{-1} in THF at 50°C.

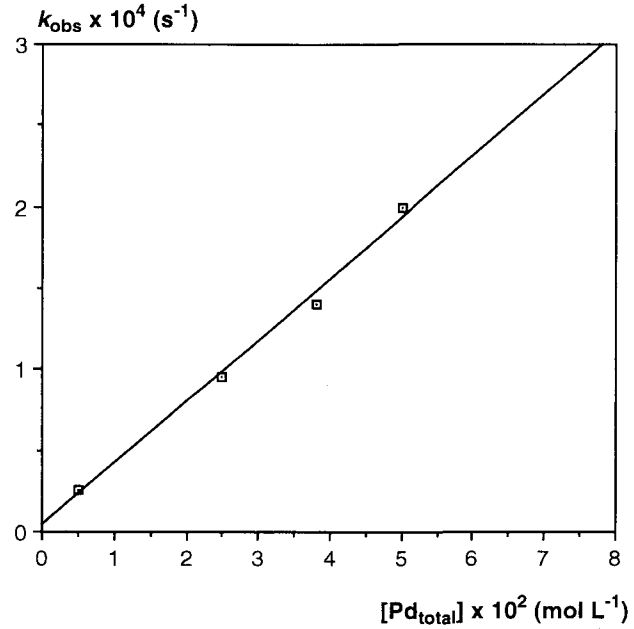


Figure 4. Variation of the pseudo-first-order rate constant (k_{obs}) with the total palladium concentration.

$$-d[PhSnBu_3]/dt = k_2[PhSnBu_3][Pd_{total}] \qquad (7)$$

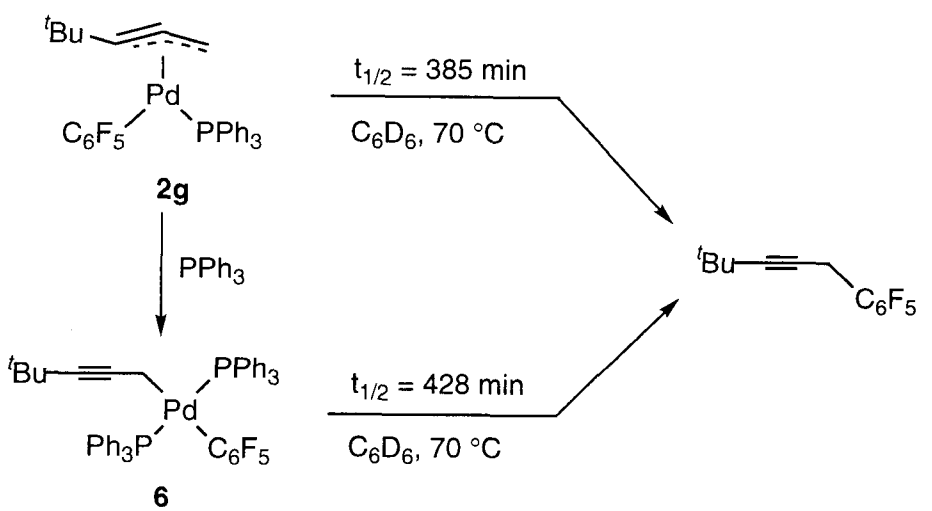
Significantly, NMR examination of the catalytic reaction mixture confirmed that complex **4** is the resting state species, indicating transmetalation is the rate-determining step of the catalysis. An analogous conclusion involving rate-determining transmetalation from organotins to $Pd(Ph)(I)(L)_2$ has been reached previously for Pd-catalyzed cross-coupling between PhI and CH_2=$CHSnBu_3$.[16]

I further assume that the transmetalation step in Scheme 4, namely, the reaction between $PhSnBu_3$ and bisphosphine complex **5**, is considerably slower than that in Scheme 3 between $PhSnBu_3$ and monophosphine complex **4**, resulting in the less efficient overall cross-coupling using the catalyst system PPh_3/Pd = 4/1. The difference between the rates of the transmetalation involving **4** and **5** would be rationalized by the different

steric congestion about the Pd atom; two molecules of PPh_3 in **5** may induce much more severe congestion during the transmetalation than a single PPh_3 ligand in **4**. Although the transfer of Ph from $PhSnBu_3$ to **5** may be quite slow, we presume the transmetalation between $PhC{\equiv}CSnBu_3$ and **5** is not so sluggish in view of the less bulky, and more negative nature of the C≡CPh group than the Ph group and the propensity of the former to form a π-complex to assist the subsequent transmetalation step. Such facilitation of the transmetalation by π-complex formation has been suggested for the vinyl transfer from $CH_2{=}CHSnBu_3$ to palladium.[16]

More support for the intervention of the η^3-allenyl/propargyl complex in cross-coupling came from the synthesis and thermolysis of the phenylated intermediate model, $Pd(\eta^3\text{-}^t BuC{\equiv}CCH_2)(C_6F_5)(PPh_3)$ (**2g**). Thus, heating a C_6D_6 solution of **2g** afforded a good yield of $^t BuC{\equiv}CCH_2C_6F_5$ (Scheme 5) possibly via geometrical isomerization to a complex having the CH_2 terminal and C_6F_5 *cis* to each other.[17] Note also that **2g** and $Pd(\eta^1\text{-}CH_2C{\equiv}CBu^t)(C_6F_5)(PPh_3)_2$ (**6**) were found to undergo reductive elimination at comparable rates (Scheme 5), suggesting that the steps after transmetalation in both Scheme 3 and 4 are comparably fast.

Scheme 5



2-7 Conclusion

I described the synthesis and characterization of the equilibrium mixture of neutral η^3-allenyl/propargylpalladium complex and η^1-propargylpalladium halide dimer. It was possible to control η^3-propargyl coordination on mononuclear palladium center by appropriate choice of substituent R on the propargyl ligand, ligand X on Pd, solvent and amount of PPh_3 attached to Pd. In addition, these type complexes are more effective intermediates in Pd-catalyzed regioselective cross-coupling between propargyl electrophiles and organotin reagents.

2-8 Experimental Section

General Procedures.

Most of commercially available reagents were used without further purification. All reactions and manipulations of air- and moisture-sensitive compounds were carried out under an atmosphere of dry Ar by use of standard vacuum line techniques. Melting points were determined on a Yanagimoto 1493 micro melting point apparatus. Molecular weights were measured on a Corona 114 molecular weight apparatus. NMR spectra were obtained on JEOL GSX-270, JEOL GSX-400 and Bruker AM 600 spectrometers. Chemical shifts are given in ppm using TMS or H_3PO_4 as standard. Single crystal X-ray structure determinations were carried out on a Rigaku AFC5R diffractometer. GLC analyses (25 m × 0.2 mm CBP1-M25-0.25 capillary column) were performed with a flame ionization detector and He carrier gas.

All of the solvents were distilled prior to use. Most commercially available reagents were used without further purification. $RC{\equiv}CCH_2OH$[18] (R = ^{t}Bu, $(CH_3)_3Si$, ^{t}Bu$(CH_3)_2Si$, ^{i}Pr$_3$Si), $Pt(C_2H_4)(PPh_3)_4$[19] were prepared according to the published methods. Chlorination of $RC{\equiv}CCH_2OH$ (R = ^{t}Bu, $(CH_3)_3Si$, ^{t}Bu$(CH_3)_2Si$, ^{i}Pr$_3$Si) was carried out according to a literature procedure.[20]

Preparation of Pd(^{t}BuCCCH$_2$)(Cl)(PPh$_3$) (2a).

To a dry CH_2Cl_2 solution (3.0 mL) of 64.5 mg (0.0623 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$ and 32.7 mg (0.125 mmol) of PPh_3 was added 16.3 mg (0.125 mmol) of ^{t}BuC≡CCH$_2$Cl (**1a**) under an argon atmosphere. After 2 h, the reaction mixture was purified by column (silica gel, 100-200 mesh, CH_2Cl_2, Rf = 0.19), and recrystallization from CH_2Cl_2-hexane gave yellow crystals of **2a** (52.5 mg, 84%) mp 119-123 °C (dec.); Anal. Calcd for $C_{25}H_{26}ClPPd$: C, 60.14; H, 5.25. Found: C, 59.99; H, 5.39. Molecular weights found by vapor pressure osmometry in chroloform at 35 °C were 513 and 500 at concentrations 2.40 × 10^{-3} and 1.02 × 10^{-2} M; calcd for monomer 499 and dimer 999.

η^3-type monomer: ^{1}H NMR ($CDCl_3$) δ 1.51 (s, 9H), 2.23 (d, J_{PH} = 1.5 Hz, 2H), 7.37-7.46 (m, 9H), 7.63-7.68 (ddd, J_{HH} = 7.7, 2.0 Hz, J_{PH} = 12.0 Hz, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 36.70 (s, CCH_2), 79.26 (d, J_{PC} = 6.0 Hz CCH_2), 118.68 (d, J_{PC} = 40.0 Hz, ^{t}BuCC); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 29.13.

Preparation of Pd(Me$_3$SiCCCH$_2$)(Cl)(PPh$_3$) (2b).

The procedure was similar to that for **2a**. Yield 84%; mp 161-163 °C (dec.); Anal. Calcd for $C_{24}H_{26}ClPPdSi$: C, 55.93; H, 5.08. Found: C, 56.20; H, 5.17.

η^3-type monomer: ^{1}H NMR ($CDCl_3$) δ 0.43 (s, 9H), 2.30 (s, 2H), 7.35-7.49 (m, 9H), 7.61-7.73 (m, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 36.59 (s, CCH_2), 102.25 (s, CCH_2), 107.82 (d, J_{PC} = 33.6 Hz, SiCC); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 30.05.

Preparation of Pd(^{t}Bu(Me)$_2$SiCCCH$_2$)(Cl)(PPh$_3$) (2c).

The procedure was similar to that for **2a**. Yield 46%; mp 150-153 °C (dec.); Anal. Calcd for $C_{27}H_{32}ClPPdSi$: C, 58.17; H, 5.79. Found: C, 58.00; H, 5.76.

η^3-type monomer: ^{1}H NMR ($CDCl_3$) δ 0.40 (s, 6H), 0.99 (s, 9H), 2.29 (s, 2H), 7.38-7.47 (m, 9H), 7.63-7.68 (dd, J_{HH} = 7.5 Hz, J_{PH} = 11.7 Hz, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 36.42 (s, CCH_2), 102.34 (s, CCH_2), 105.99 (d, J_{PC} = 29.7 Hz, SiCC); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 29.40.

η^1-type dimer: ^{1}H NMR ($CDCl_3$) δ -0.01 (s, 6H), 0.98 (s, 9H), 1.96 (s, 2H), 7.28-7.50

(m, 9H), 7.57-7.89 (m, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 7.34 (s, CCH_2), 88.06 (s, CCH_2), 111.78 (s, Si*C*C); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 34.48.

Preparation of Pd(^{i}Pr$_3$SiCCCH$_2$)(Cl)(PPh$_3$) (2d).

The procedure was similar to that for **2a**. Yield 84%; mp 196-200 °C (dec.); Anal. Calcd for $C_{30}H_{38}ClPPdSi$: C, 60.10; H, 6.39. Found: C, 60.33; H, 6.54. Molecular weights found by vapor pressure osmometry in chroloform at 35 °C were 643, 681, and 717 at concentrations 3.67×10^{-3}, 8.17×10^{-3}, and 1.20×10^{-2} M; calcd for monomer 600 and dimer 1199.

η^3-type monomer: ^1H NMR ($CDCl_3$) δ 1.15 (d, J_{HH} = 7.3 Hz, 18H), 1.49 (sept, J_{HH} = 7.3 Hz, 3H), 2.25 (s, 2H), 7.28-7.52 (m, 9H), 7.55-7.84 (m, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 35.64 (s, CCH_2), 104.19 (s, CCH_2), 105.17 (d, J_{PC} = 35.3 Hz, Si*C*C); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 30.72.

η^1-type dimer: ^1H NMR ($CDCl_3$) δ 0.99 (sept, J_{HH} = 5.3 Hz, 3H), 1.04 (d, J_{HH} = 5.3 Hz, 18H), 1.95 (s, 2H), 7.28-7.52 (m, 9H), 7.55-7.84 (m, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 8.10 (s, CCH_2), 86.35 (s, CCH_2), 112.70 (s, Si*C*C); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 35.44.

Preparation of Pd(^{i}Pr$_3$SiCCCH$_2$)(Br)(PPh$_3$) (2e).

To a dry CH_2Cl_2 solution (2.0 mL) of 115 mg (0.111 mmol) of $Pd_2(dba)_3{\cdot}CHCl_3$ and 58.1 mg (0.222 mmol) of PPh_3 was added 56.3 mg (0.244 mmol) of $^iPr_3SiC{\equiv}CCH_2Cl$ (**1d**) under an argon atmosphere. After 2 h, to the reaction mixture was added a methanol solution of 34.2 mg (0.332 mmol) of NaBr. After 3 min, the reaction mixture was concentrated in vacuo, and the residues dissolved in CH_2Cl_2 were filtered. The filtrate was evaporated, and recrystallization from CH_2Cl_2-ether-hexane gave yellow crystals of **2e** (80.6 mg, 56%); mp 126-129 °C (dec.); Anal. Calcd for $C_{30}H_{38}BrPPdSi$: C, 55.95; H, 5.95. Found: C, 55.79; H, 5.99.

η^3-type monomer: ^1H NMR ($CDCl_3$) δ 1.15 (d, J_{HH} = 7.8 Hz, 18H), 1.53 (sept, J_{HH} = 7.8 Hz, 3H), 2.37 (s, 2H), 7.32-7.48 (m, 9H), 7.63-7.73 (m, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ

38.79 (s, CCH_2), 103.96 (d, J_{PC} = 37.9 Hz, Si*C*C), 105.18 (s, CCH_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 31.02.

η^1-type dimer: ^1H NMR ($CDCl_3$) δ 1.06 (s, 21H), 2.03 (s, 2H), 7.32-7.48 (m, 9H), 7.43-7.73 (m, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 9.33 (s, CCH_2), 86.76 (s, CCH_2), 112.84 (s, Si*C*C); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 35.49.

Preparation of Pd(^{i}Pr$_3$SiCCCH$_2$)(I)(PPh$_3$) (2f).

The procedure was similar to that for **2e**. Yield 61%; mp 174-177 °C (dec.); Anal. Calcd for $C_{30}H_{38}IPPdSi$: C, 52.14; H, 5.54. Found: C, 51.98; H, 5.51. Molecular weights found by vapor pressure osmometry in chroloform at 35 °C were 695 and 698 at concentrations $2.80x10^{-3}$ and $1.99x10^{-2}$ M; calcd for monomer 691 and dimer 1382.

η^3-type monomer: ^1H NMR ($CDCl_3$) δ 1.14 (d, J_{HH} = 7.3 Hz, 18H), 1.59 (sept, J_{HH} = 7.3 Hz, 3H), 2.64 (d, J_{PH} = 2.19 Hz, 2H), 7.34-7.48 (m, 9H), 7.66 (ddd, J_{PH} = 11.7 Hz, J_{HH} = 7.8 Hz, J_{HH} = 2.0 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 44.07 (s, CCH_2), 100.88 (d, J_{PC} = 39.1 Hz, Si*C*C), 107.36 (s, CCH_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 31.05.

Preparation of Pd(η^3-^{t}BuCCCH$_2$)(C$_6$F$_5$)(PPh$_3$) (2g).

To a THF solution (1.0 mL) of pentafluorophenyllithium, which was obtained from 84.4 mg (0.502 mmol) of pentafuluorobenzene and an equimolar amount of commercial *n*-butyllithium, was added dropwise a solution of 125.4 mg (0.251 mmol) of **2a** in THF (3.0 mL) under argon atmosphere at -73 °C. Stirring at this temperature was continued for 1 h. The reaction mixture was allowed to warm to -20 °C and 0.3 mL of MeOH added. The reaction mixture was allowed to warm to room temperature and the solvent was removed in vacuum. The yellow residue was purified by chromatography through a short Florisil column. Recrystallization from toluene-hexane gave light yellow crystal of **2g** (81.7 mg, 52%) mp 145-148 °C (dec.); Anal. Calcd for $C_{31}H_{26}F_5PPd$: C, 59.01; H, 4.15. Found: C, 59.30; H, 4.13. Molecular weights found by vapor pressure osmometry in chroloform at 35 °C were 638 and 635 at concentrations 1.08×10^{-2} and 3.39×10^{-2} M; calcd for

monomer 631.

η^3-type monomer: ^{1}H NMR ($CDCl_3$) δ 1.16 (s, 9H), 2.78 (d, J_{PH} = 1.3 Hz, 2H), 7.29-7.43 (m, 15H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 43.80 (s, CCH_2), 93.15 (d, J_{PC} = 4.7 Hz, CCH_2), 114.25 (d, J_{PC} = 55.2 Hz, ^{t}BuCC); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 34.12.

Reaction of 2g with $Pt(C_2H_4)(PPh_3)_2$.

A CH_2Cl_2 solution (2.0 mL) of **2g** (35.5 mg; 0.0563 mmol) and $Pt(C_2H_4)(PPh_3)_2$ (46.8 mg; 0.0626 mmol) was stirred for 2 h at 25 °C. The reaction mixture was purified by chromatography through a short Florisil column. Recrystallization from CH_2Cl_2-hexane gave light yellow crystal of **3g** (56.8 mg, 75%) mp 155-158 °C (dec.); Anal. Calcd for $C_{67}H_{56}F_5P_3PdPt(CH_2Cl_2)_{0.5}$: C, 58.20; H, 4.12. Found: C, 58.57; H, 4.17.; ^{1}H NMR ($CDCl_3$) δ 0.77 (s, 9H), 2.87 (d, J_{PH} = 7.8, J_{PtH} = 70.0 Hz, 1H), 2.94 (d, J_{PH} = 18.9, J_{PtH} = 79.3 Hz, 1H), 6.86-7.80 (m, 45H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 50.14 (s, CCH_2), 108.98 (d, J_{PC} = 70.3 Hz, J_{PtC} = 338.4 Hz, CCH_2), 112.62 (dd, J_{PC} = 72.6 Hz, 39.2 Hz, J_{PtC} = 338.0 Hz, ^{t}BuCC); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 22.01 (d, J_{PP} = 28.5 Hz, J_{PtP} = 3155.7 Hz), 26.49 (d, J_{PP} = 28.5 Hz, J_{PPt} = 3419.9 Hz), 27.89 (s, J_{PtP} = 41.9 Hz).

Preparation of $Pd(\eta^3$-^{t}BuCHCHCH$_2$)(C_6F_5)(PPh_3).

To a dry CH_2Cl_2 solution (15.0 mL) of 425 mg (0.410 mmol) of $Pd_2(dba)_3$·$CHCl_3$ was added 160 mg (0.902 mmol) of ^{t}BuCHCHCH$_2$Br under an argon atmosphere. After 1.5 h, the product was isolated by column (silica gel, 100-200 mesh, CH_2Cl_2), and the first eluent of yellow band was concentrated to give **$[Pd(\eta^3$-^{t}BuCHCHCH$_2$)Br$]_2$** (203 mg, 87%), which was not further purified. ^{1}H NMR ($CDCl_3$) δ 1.19 (s, 9H), 2.81 (d, J_{HH} = 11.7 Hz, 1H), 3.93 (d, J_{HH} = 6.8 Hz, 1H), 3.98 (d, J_{HH} = 11.7 Hz, 1H), 5.25 (ddd, J_{HH} = 11.7, 11.7, 6.8 Hz, 1H). To a THF solution (1.0 mL) of pentafluorophenyllithium, which was obtained from 195 mg (1.16 mmol) of pentafuluorobenzene and an equimolar amount of commercial *n*-butyllithium, was added dropwise a solution of 165 mg (0.290 mmol) of **$[Pd(\eta^3$-^{t}BuCHCHCH$_2$)Br$]_2$** and 152 mg (0.581 mmol) of PPh_3 in THF (2.0 mL) under argon atmosphere at -73 °C. Stirring at this temperature was continued for 1 h. The

reaction mixture was allowed to warm to -20 °C and 0.5 mL of MeOH added. The reaction mixture was allowed to warm to room temperature and the solvent was removed in vacuum. The yellow residue was purified by chromatography through a short Florisil column. Recrystallization from CH_2Cl_2-hexane gave white crystal of **Pd(η^3-^{t}BuCHCHCH$_2$)(C$_6$F$_5$)(PPh$_3$)** (147.0 mg, 40%) mp 169-172 °C (dec.); Anal. Calcd for $C_{31}H_{28}F_5PPd$: C, 58.83; H, 4.46. Found: C, 58.80; H, 4.27.; ^{1}H NMR ($CDCl_3$) δ 0.92 (s, 9H), 2.30 (d, J_{HH} = 12.2 Hz, 1H), 3.45 (d, J_{HH} = 7.3 Hz, 1H), 4.21 (dd, J_{HH} = 12.7 Hz, J_{PH} = 10.3 Hz, 1H), 5.33 (ddd, J_{HH} = 12.7, 12.2, 7.3 Hz, 1H), 7.19-7.39 (m, 15H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 59.39 (s, *C*CH$_2$), 104.12 (d, J_{PC} = 33.4 Hz, ^{t}Bu*C*C), 113.09 (s, *C*CH$_2$); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 29.65.

Single crystal X-ray diffraction study.

All data were obtained on a Rigaku AFC-5R diffractometer with graphite-monochromated Mo-Kα radiation. All calculations were carried out with the TEXSAN crystallographic software package of Molecular Structure Corporation. The structure was solved by the direct method and refined by the full-matrix least-squares procedure, the function minimized being $\Sigma w(|F_o|-|F_c|)^2$. The non-hydrogen atoms were refined anisotropically. All the positions of the hydrogen atoms were calculated by stereochemical considerations.

Pd(^{i}Pr$_3$SiCCCH$_2$)(Cl)(PPh$_3$) (2d).

A yellow crystal (0.20 × 0.30 × 0.40 mm) was obtained from CH_2Cl_2/hexane at -30 °C and was mounted on a glass fiber with epoxy resin. $C_{30}H_{38}ClPPdSi$, M = 599.54, triclinic, space group $P\bar{1}$*(#2)*, *a* = 10.448(5) Å, *b* = 16.724(6) Å, *c* = 8.935(3) Å, α = 98.22(3)°, β = 96.16(3)°, γ = 95.79(4)°, *V* = 1525(1) Å^3, *Z* = 1, D_{calc} = 0.653 g/cm^3, *F*(000) = 310.00, μ(Mo-Kα) = 4.02 cm^{-1} by least squares refinement on diffractometer angles from automatically centered reflections, 2θ range 27.20-27.46°, λ = 0.71069 Å. The final *R* and R_w values were 0.039 and 0.045, respectively, for 5685 reflections (I > 3.00σ(I)).

Pd(^{t}BuCCCH$_2$)(C$_6$F$_5$)(PPh$_3$) (2g).

A yellow crystal (0.50 × 0.30 × 0.50 mm) was obtained from CH_2Cl_2/hexane at -30

°C and was mounted on a glass fiber with epoxy resin. $C_{31}H_{26}F_5PPd$, M = 630.91, triclinic, space group $P\bar{1}$(#2), a = 16.56(3) Å, b = 18.00(4) Å, c = 11.141(9) Å, α = 101.1(1)°, β = 107.5(1)°, γ = 63.5(2)°, V = 2828(9) Å^3, Z = 4, D_{calc} = 1.481 g/cm^3, F(000) = 1272.00, μ(Mo-Kα) = 7.64 cm^{-1} by least squares refinement on diffractometer angles from automatically centered reflections, 2θ range 27.39-27.49°, λ = 0.71069 Å. The final R and R_w values were 0.057 and 0.047, respectively, for 9164 reflections (I > 3.00σ(I)).

$(PPh_3)_2Pt(\mu\text{-}\eta^2\text{:}\eta^3\text{-}^t BuCCCH_2)Pd(C_6F_5)(PPh_3)$ (3g).

A yellow crystal (0.40 × 0.40 × 0.50 mm) was obtained from CH_2Cl_2/hexane at -30 °C and was mounted on a glass fiber with epoxy resin. $C_{67}H_{56}F_5P_3PdPt$, M = 1350.58, monoclinic, space group $P2_1/n$(#14), a = 14.642(4) Å, b = 19.042(4) Å, c = 20.964(3) Å, β = 101.85(2)°, V = 5720(2) Å^3, Z = 4, D_{calc} = 1.568 g/cm^3, F(000) = 2688.00, μ(Mo-Kα) = 29.16 cm^{-1} by least squares refinement on diffractometer angles from automatically centered reflections, 2θ range 27.32-27.51°, λ = 0.71069 Å. The final R and R_w values were 0.048 and 0.028, respectively, for 8776 reflections (I > 3.00σ(I)).

Coupling reaction with tin compounds by using $Pd_2(dba)_3$·$CHCl_3$-PPh_3 (Pd/PPh_3 = 1/1) catalyst (Method A) and $Pd(PPh_3)_4$ catalyst (Method B).

Method A: At room temperature and under an argon atmosphere, propargyl chloride (0.50 mmol) was added to a solution of $Pd_2(dba)_3CHCl_3$ (0.0125 mmol) and PPh_3 (0.025 mmol) in dry THF (1 ml). The mixture was stirred for 40 min to give a yellow solution. The tin compound (0.55 mmol) was added to the solution and the mixture was heated to 50 °C. The reaction was followed by GLC.

Method B: At room temperature and under an argon atmosphere, propargyl chloride (0.50 mmol) and the tin compound (0.55 mmol) were added to a solution of $Pd(PPh_3)_4$ (0.025 mmol) in dry THF (1 ml). The mixture was heated to 50 °C. The reaction was followed by GLC.

Purification of the major coupling products was performed as shown below, while the

minor products in Table 2 were observed only by GLC.

PhC≡CC(^{t}Bu)=C=CH$_2$.

The reaction mixture starting from ^{t}BuC≡CCH$_2$Cl (**1a**) and PhC≡CSnBu$_3$ in THF was washed with an aqueous NH_4F (15%) and extracted three times with ether. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The concentrate was distilled to give **PhC≡CC(^{t}Bu)=C=CH$_2$** (b.p. 120 °C/4 mmHg) in 65% isolated yield. ^{1}H NMR ($CDCl_3$) δ 1.19 (s, 9H), 5.03 (s, 2H), 7.2-7.5 (m, 5H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 29.11, 33.98, 78.11, 83.45, 93.03, 100.42, 123.67, 127.90, 128.21, 131.31, 211.81.; HRMS Calcd for $C_{15}H_{16}$ 196.1252, Found: *m/e* 196.1243.

^{t}BuC≡CCH$_2$Ph.

B.p. 90 °C/4 mmHg (68% isolated yield). ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 9H), 3.58 (s, 2H), 7.10-7.50 (m, 5H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 24.95, 27.47, 31.30, 75.81, 91.37, 126.28, 127.73, 128.32, 137.66.; HRMS Calcd for $C_{13}H_{16}$ 172.1252, Found: *m/e* 172.1269. **Ph(^{t}Bu)C=C=CH$_2$** could not be separated from the product mixture containing **^{t}BuC≡CCH$_2$Ph**. ^{1}H NMR ($CDCl_3$) δ 4.18 (s, 2H, CH_2=); MS found *m/e* 172 (M^+), 157 (M^+ - CH_3), 115 (M^+ - ^{t}Bu).

Me$_3$SiC≡CCH$_2$Ph.

B.p. 90-93 °C/1 mmHg; ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 9H), 3.67 (s, 2H), 7.20-7.40 (m, 5H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 0.06, 26.15, 70.45, 86.87, 126.55, 127.85, 128.47, 136.34.

Me$_3$SiC≡CCH$_2$Ph was identical with the known compound. (Registry No. 31683-47-3)

Observation of 4 as a resting-state intermediate in a catalytic reaction.

Under an argon atmosphere, to a solution of **4** (**2a**) (R = ^{t}Bu, 0.0038 mmol) in dry C_6D_6 (0.6 ml) were added ^{t}BuC≡CCH$_2$Cl (0.038 mmol) and PhSnBu$_3$ (0.041 mmol) at room temperature. The mixture was heated at 50 °C for 24 h during which the

intermediate **2a** was confirmed by ^{1}H NMR spectra as a predominant species at earlier stages (approximately 1 h), but gradual decrease of this complex occurred due to increasing decomposition of catalyst complexes.

Rates of coupling reaction.

Under an argon atmosphere, ^{t}BuC≡CCH$_2$Cl (0.55 mmol) was added to a solution of a given amount (catalytic) of $Pd_2(dba)_3$·$CHCl_3$ and PPh_3 (Pd/PPh_3 = 1/1) in dry THF (1 ml). The mixture was stirred for 40 min causing a gradual change in color from dark-purple to yellow. Then, $PhSnBu_3$ (0.55 mmol) was added and the mixture was heated to 50 °C. The reaction was followed by determination of the concentration of the propargyl chloride (RCl) by GLC. I assumed [RCl] = [$PhSnBu_3$], and then plots of ln[$PhSnBu_3$] versus time gave straight lines whose slopes corresponded to k_{obs} where rate = k_{obs}[$PhSnBu_3$]. [Pd] = 5.0×10^{-3} M, k_{obs} = 2.6×10^{-5} s^{-1}. [Pd] = 2.5×10^{-2} M, k_{obs} = 9.5×10^{-5} s^{-1}. [Pd] = 3.8×10^{-2} M, k_{obs} = 1.4×10^{-4} s^{-1}. [Pd] = 5.0×10^{-2} M, k_{obs} = 2.0×10^{-4} s^{-1}. Then plotting k_{obs} versus [Pd] gave a straight line passing through the origin within an acceptable error range (Fig 4), affording the second-order rate constant, k_2 = 3.8×10^{-3} M^{-1}s^{-1} where the rate = k_2[$PhSnBu_3$][Pd].

Rates of reductive elimination from 2g.

A solution of **2g** (0.00396 mmol) in dry C_6D_6 (0.5 mL) was heated at 70 °C and the reaction was followed by ^{1}H NMR spectra. k = 3.0×10^{-5} s^{-1}, $t_{1/2}$ = 385 min. **2g** was decomposed to generate **^{t}BuC≡CCH$_2$C$_6$F$_5$**.

^{t}BuC≡CCH$_2$C$_6$F$_5$; ^{1}H NMR ($CDCl_3$) δ 1.14 (s, 9H), 3.11 (s, 2H). This compound was not isolated.

Rates of reductive elimination from 6.

A solution of **6** in dry C_6D_6 (0.5 mL) was prepared from the reaction of **2g** (0.00697 mmol) and PPh_3 (0.0278 mmol) in situ and was heated at 70 °C. The reaction was followed by ^{1}H NMR spectra. k = 2.7×10^{-5} s^{-1}, $t_{1/2}$ = 428 min.

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(5) Prepared similarly to the trimethylsilyl analog reported in Ref 4. ^{13}C NMR ($CDCl_3$) δ 7.87 (s, CCH_2), 85.55 (s, CCH_2), 111.80 (s, Si*C*C).

(6) VPO molecular weights of **2a** and **2f** in chloroform at 35 °C were 500 at $1.02x10^{-2}$ M (calcd for monomer, 499); and 698 at $1.99x10^{-2}$ M (calcd for monomer, 691), respectively.

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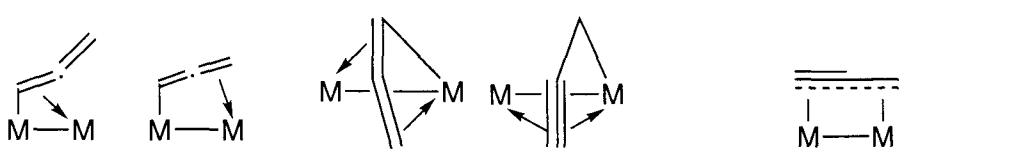
Chapter 3

μ-η^3-Allenyl/propargyldipalladium complexes

3-1 Introduction

Polynuclear organotransition-metal compounds are expected to have specific reactivities and chemical properties not observed in mononuclear complexes and serve as models of the metal surface-hydrocarbon interaction. Recently, polyhapto allenyl and propargyl dimetal complexes have been shown to possess the various bonding structures.[1] Typical examples include μ-allenyl/propargyl dinuclear complexes (type A (η^2, 4e)[2] or type B (η^3, 6e)[3]) (Scheme 1).[4] Geometrically, the inherently linear unsaturated hydrocarbon framework might match a linear dinuclear moiety better than a mononuclear moiety, but only one example of such type has been reported in Ru_2 and Os_2 systems (A').[5] There has been no example of type C complex having such a more delocalized structure through resonance of η^3-allenyl and η^3-propargyl forms. Little has been reported on the chemical reactivity of the above polynuclear complexes. Type A complexes reacted with nucleophiles, forming saturated and unsaturated metallacycles via exclusive nucleophilic attack at central carbon of allenyl ligand.[5a] Other mononuclear allenyl/propargyls also show a propensity for attack at central carbon.[6]

Scheme 1



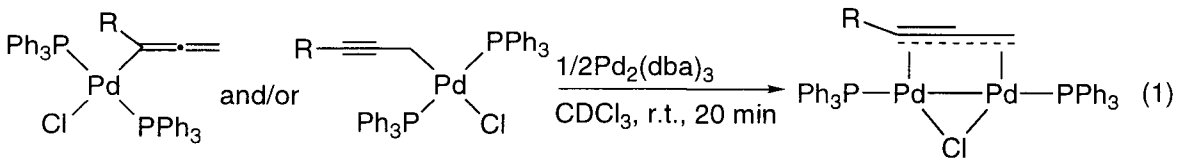
μ-allenyl	μ-allenyl	μ-allenyl	μ-propargyl	μ-η^3-allenyl/propargyl
(η^2, 4e)	(η^3, 4e)	(η^3, 6e)	(η^3, 6e)	(η^3, 4e)
A	A'	B		C

In this chapter, I report synthesis, structure and reactivity of type C complexes of

palladium. In addition, the structure and reactivity of μ-vinylcarbene dipalladium complexes generated from the reaction of η^3-allenyl/propargyldipalladium complexes with electrophiles are also discussed.

3-2 Synthesis and property of μ-η^3-allenyl/propargyldipalladium complexes.

The reaction of η^1-allenyl or η^1-propargyl bistriphenylphosphine palladium chloride (**1a-d**)[8] with $Pd_2(dba)_3 \cdot CHCl_3$ in $CDCl_3$ at room temperature gave μ-η^3-allenyl/propargyldipalladium complexes (**2a-d**) (eq. 1). The analogous reaction of **1b** in the presence of NaI and NaSPh gave the iodide and phenyl thiolate analogs, respectively (**2b-I** 63%, **2b-SPh** 78%). The ^{31}P NMR spectrum of **2** showed two signals with large phosphorus-phosphorus coupling ($J_{PP} \geq 80$ Hz). Addition of PPh_3 to **2a-d** led to regeneration of **1a-d** as well as generation of $Pd(PPh_3)_2$.

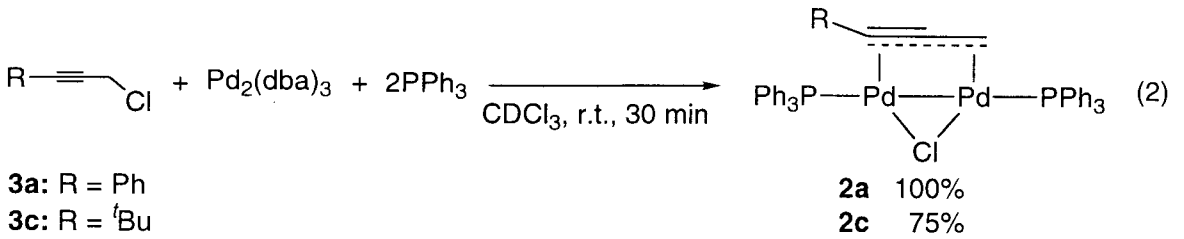


(1)

1a: R = Ph (allenyl : propargyl = 75 : 25)
1b: R = $SiMe_3$ (propargyl)
1c: R = ^{t}Bu (propargyll)
1d: R = H (allenyl)

2a 100%
2b 85%
2c 84%
2d 29%

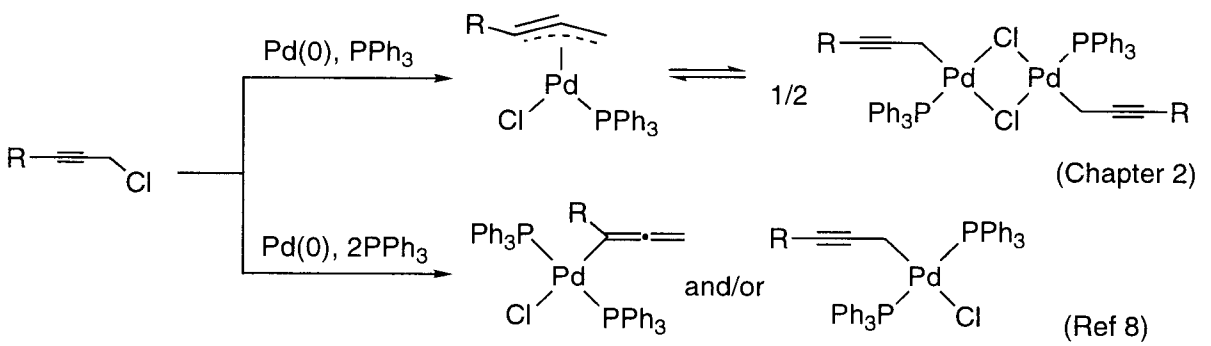
The complexes **2** also could be obtained from the reaction of corresponding propargyl chloride **3** with 2 equiv of $Pd(PPh_3)$ generated in situ (eq. 2). On the other hand, treatment of 1 equiv of $Pd(PPh_3)$ led to formation of the equilibrium mixture of neutral η^3-allenyl/propargylpalladium monomer and η^1-propargylpalladium chloride dimer (Scheme 2, see Chapter 2). The preparation of η^1-allenyl and η^1-propargylpalladium complexes is known from $Pd(PPh_3)_4$ (Scheme 2, see Ref 8). Thus, these reactions constitute general synthetic routes to palladium complexes containing η^1- and η^3-allenyl/propargyl ligand.



3a: R = Ph
3c: R = ^{t}Bu

2a 100%
2c 75%

Scheme 2



3-3 X-ray structure of μ-η^3-allenyl/propargyldipalladium complexes

The structures of dinuclear complexes **2d** and **2a-SPh** are presented in Figures 1 and 2. The μ-η^3-allenyl/propargyl group is almost linear (C1-C2-C3 = 178(2)° in **2c**, 173.2(3)° in **2a-SPh**), in contrast to that of η^3-allenyl/propargyl mononuclear complexes (Pd,[6c] Pt,[6d,g] Mo[9a], Zr,[9b,c] Re[9d] and see Chapter 1 and 2) and other μ-allenyl or μ-propargyl dinuclear complexes (type A,[2a] B[3a,5b]) having bent C-C-C units, and parallels the Pd-Pd bond. Thus, the Pd1-C1 distance (2.06(2) Å, 2.066(3) Å) is almost equal to the Pd2-C3 distance (2.08(2) Å, 2.096(3) Å). Moreover, the Pd-Pd distance (2.642(2) Å, 2.6291(4) Å) is almost equal to the C1-C3 distance (2.69 Å, 2.663 Å). Two palladiums, η^3-allenyl/propargyl carbons, chlorine or sulfur atom, and two phosphorus atoms are located on the same plane.

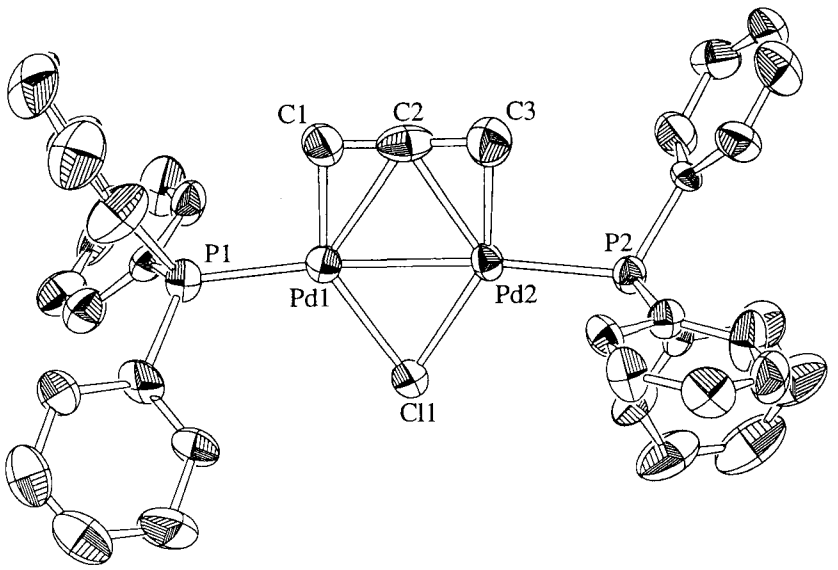


Figure 1. Molecular structure of **2b**. Selected bond distances (Å): Pd1-Pd2 = 2.642(2), Pd1-Cl = 2.405(6), Pd2-Cl = 2.397(6), Pd1-P1 = 2.252(6), Pd2-P2 = 2.282(6), Pd1-Cl = 2.06(2), Pd1-C2 = 2.47(3), Pd2-C2 = 2.42(3), Pd2-C3 = 2.08(2), C1-C2 = 1.33(3), C2-C3 = 1.36(3). Selected angle (deg): C1-C2-C3 = 178(2).

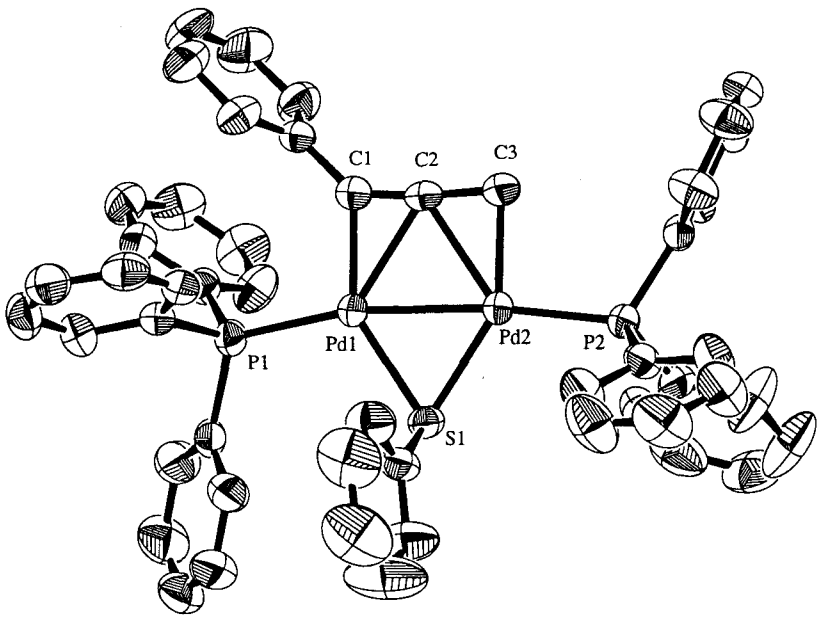
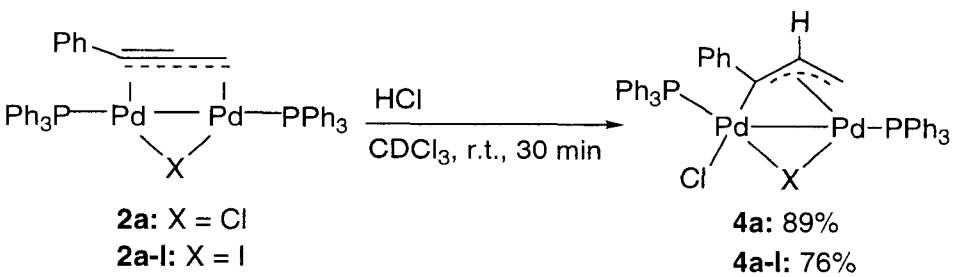


Figure 2. Molecular structure of **2a-SPh**. Selected bond distances (Å): Pd1-Pd2 = 2.6291(4), Pd1-S = 2.3621(8), Pd2-Cl = 2.3679(9), Pd1-P1 = 2.2595(9), Pd2-P2 = 2.2626(9), Pd1-Cl = 2.066(3), Pd1-C2 = 2.361(3), Pd2-C2 = 2.431(3), Pd2-C3 = 2.096(3), C1-C2 = 1.257(4), C2-C3 = 1.406(5). Selected angle (deg): C1-C2-C3 = 173.2(3).

3-4 Reaction of μ-η^3-allenyl/propargyldipalladium complexes.

The dinuclear complexes **2a** and **2a-I** reacted with HCl (generated from a reaction of H_2O with Me_3SiCl in situ) to give unusual dinuclear complexes **4a** (89%) and **4a-I** (76%) (eq. 3). The structure of **4a** was determined by X-ray diffraction (Figure 3). The structure reveals the first example of μ-vinylcarbene (or μ-η^1:η^3-allyl) complex of palladium, which is similar to μ-vinylcarbene complexes of other transition metals.[10] Further reactivities of **3** are discussed later.



2a: X = Cl
2a-I: X = I

4a: 89%
4a-I: 76%

(3)

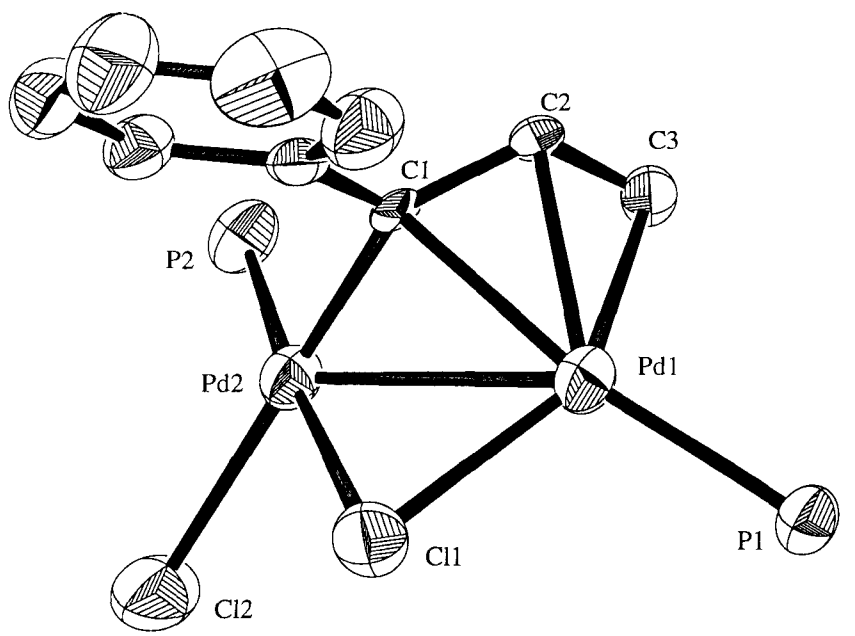
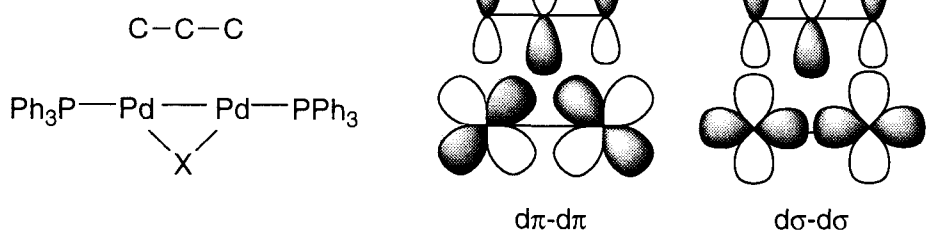


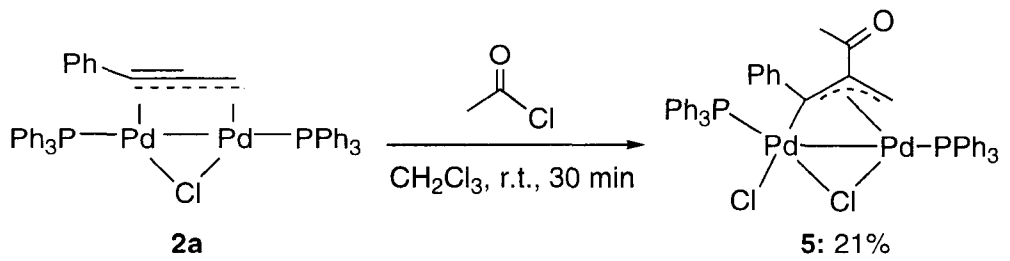
Figure 3. Molecular structure of **4a**. Selected bond distances (Å): Pd1-Pd2 = 2.868(1), Pd1-Cl = 2.425(2), Pd2-Cl1 = 2.489(2), Pd2-C1 = 2.374(3), Pd1-P1 = 2.298(2), Pd2-C2 = 2.243(2), Pd1-C1 = 2.260(8), Pd1-C2 = 2.224(9), Pd1-C3 = 2.113(10), Pd2-C1 = 2.031(9), C1-C2 = 1.40(1), C2-C3 = 1.39(1). Selected angle (deg): C1-C2-C3 = 121.9(9).

Intriguingly, in this reaction, proton added to the central carbon of η^3-allenyl/propargyl group as confirmed by the reaction with DCl, which points out occurrence of an unusual electrophilic attack at the central carbon of η^3-allenyl/propargyl group. On the other hand, in both mononuclear[6] and other dinuclear[5a] complexes, the η^3-allenyl/propargyl group is prone to be attacked by a nucleophile at the central carbon. The present unique reactivity might be due to high electron density at the central carbon (C2) in the allenyl/propargyl ligand bound on the Pd-Pd moiety as explained below. Preliminary MO calculations on $Pd_2(\mu\text{-allyl})(\mu\text{-Cl})(PH_3)_2$[11] suggest that back donation from two filled MOs of the fragment $Pd_2(\mu\text{-Cl})(PH_3)_2$ to empty π^* MO of the allyl ligand shown in Scheme 3 plays a crucial role in combining the allyl ligand to the Pd-Pd fragment. The π^* MO of the μ-allenyl/propargyl ligand is equivalent to that of the μ-allyl ligand, so that a similar back donation may be responsible for the unique structural and reactivity aspects revealed in this study. Such strong back bonding interaction can not be expected in $M_2(\mu\text{-PhC=C=CH}_2)(\mu\text{-PPh}_2)(CO)_6$ (M = Ru and Os) (type B')[5b] due to the presence of four strongly π-accepting carbon monoxide ligands which compete with the allenyl π^* MO for the $d\pi$-$d\pi$ MO of the M_2 fragment.

Scheme 3

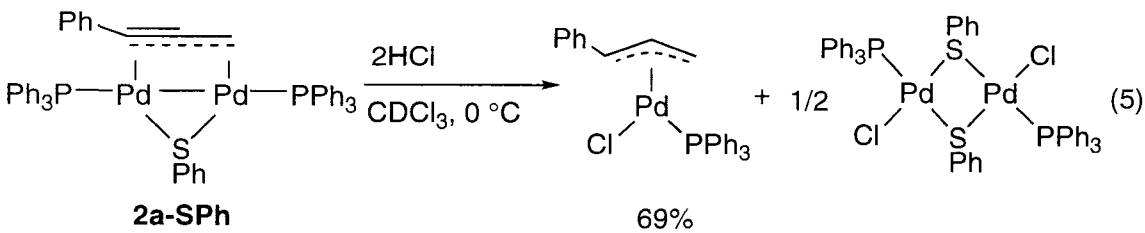


Similarly **2a** reacted with carbon electrophile acetyl chloride to generate corresponding μ-vinylcarbene complex **5** together with C-C bond formation on the central carbon of μ-η^3-allenyl/propargyl ligand (eq. 4).



(4)

The treatment of **2a-SPh** with 2 equiv of HCl led to formation of Pd(η^3-PhCHCHCH$_2$)Cl(PPh$_3$) which is a formal hydrogenation product of starting complex **1a** (eq. 5).[12] Thus, this reaction might be a model for hydrogenation reaction on a metal surface.

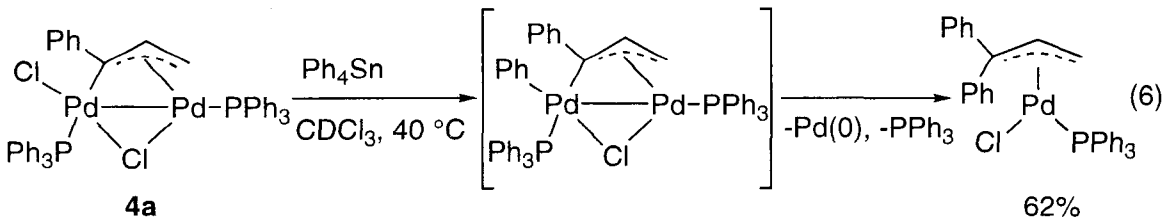


(5)

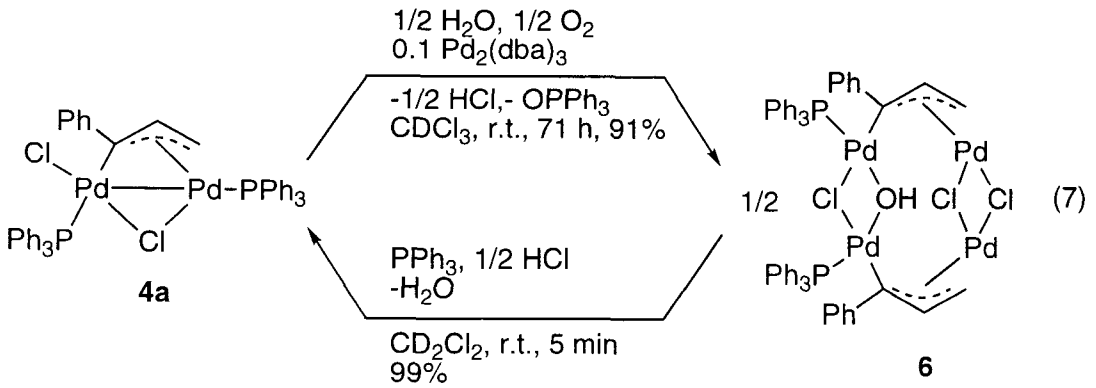
3-5 Reaction of μ-η^3-vinylcarbenedipalladium complexes

Vinylcarbene complexes of transition metals including mononuclear and dinuclear centers are becoming more common and their synthetic application has attracted increasing attention,[13] but no precedent of the reaction of vinylcarbenepalladium or even carbenepalladium complexes has been reported.[14]

In a sealed glass tube, a $CDCl_3$ solution of **4a** and Ph_4Sn was heated at 40 °C for 45 h to give η^3-1,1-diphenylallylpalladium complex (eq. 6). This complex might be generated by the reductive elimination from a phenylated dipalladium intermediate. The C-C bond coupling at dinuclear center could be a nice model for the reaction on the metal surface.[15] Mononuclear vinylcarbene complexes also react with nucleophiles to give η^3-allyl complexes.[16]



In the presence of a catalytic amount of $Pd_2(dba)_3$, the complex **4a** reacted with H_2O and O_2 to give hydroxo bridged μ-η^3-vinylcarbenedipalladium dimer **6** in excellent yield (eq. 7). The structure of the complex **6** was determined by X-ray diffraction analysis (Figure 4). This complex has a unique structure in which one of four bridging ligands is OH group. The coordination mode and geometry of μ-η^3-vinylcarbene group in **6** are quite similar to those in **4a**. However, the Pd-Pd distance in **6** (3.17 Å) is somewhat longer than in **4a** (2.87 Å), possibly reflecting the absence, in the former, of the Cl bridge on the Pd-Pd opposite to the vinylcarbene bridge. The transformation shown in eq. 7 did not work well without $Pd_2(dba)_3$ which might have a role of oxidizing PPh_3 to $O{=}PPh_3$, which was confirmed by ^{31}P NMR spectra. Treatment of **6** with PPh_3 and HCl regenerated the dimer complex **4a** quantitatively.



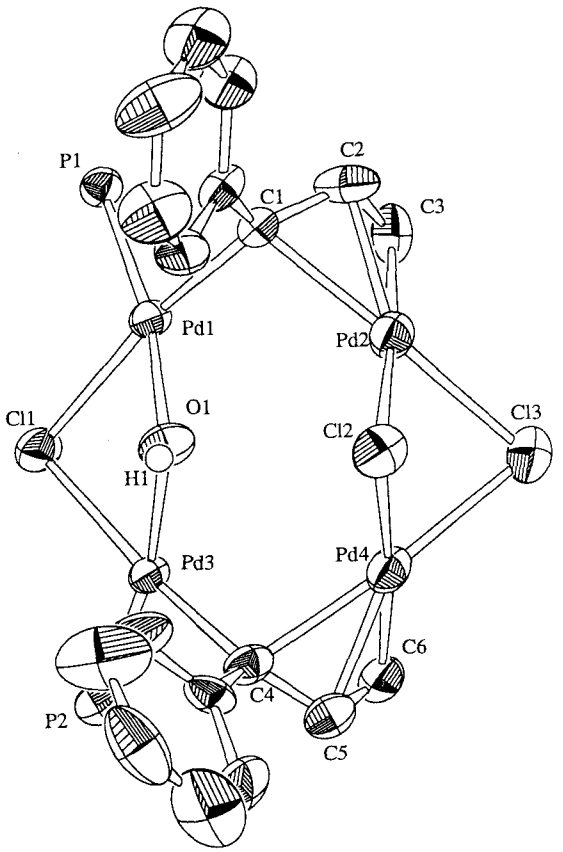
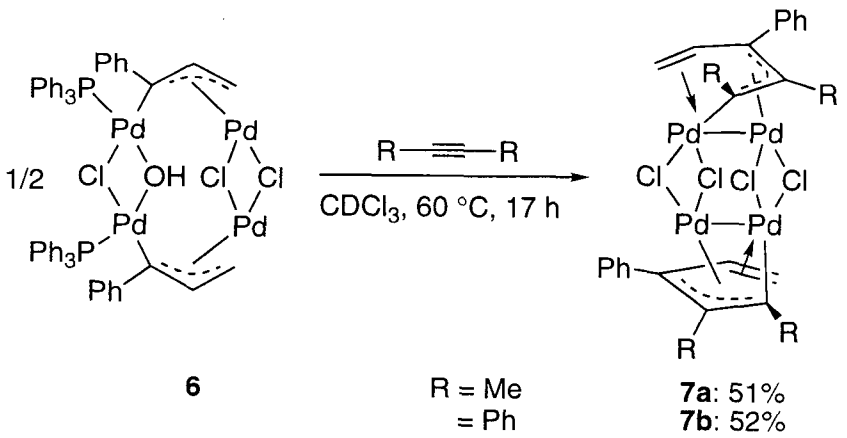


Figure 4. Molecular structure of **6**. Selected bond distances (Å): Pd1-O1 = 2.037(9), Pd1-Cl1 = 2.453(3), Pd2-Cl2 = 2.458(4), Pd2-Cl3 = 2.411(4), Pd1-C1 = 2.04(1), Pd2-C1 = 2.20(1), Pd2-C2 = 2.10(1), Pd2-C3 = 2.09(2), C1-C2 = 1.40(2), C2-C3 = 1.43(2), Pd1-Pd2 = 3.17 (non-bonding). Selected angle (deg): C1-C2-C3 = 123(1).

In a sealed glass tube, a $CDCl_3$ solution of **6** and 2.2 equiv of internal alkynes was heated at 60 °C for 17 h. The ^1H NMR spectrum of a reaction mixture showed the presence of two sets of resonances (ca. 2:1) which are similar to each other.[17] The major product was separated by recrystallization from a yellow eluent of column chromatography to give a μ-η^2:η^3-dienylcarbene complex (**7a**, **7b**) (eq 8). The structure of **7a** was determined by X-ray structure analysis, revealing that alkynes have inserted into the palladium-carbene carbon bond to form a new μ-η^3-vinylcarbene moiety[18,19] and OH group has been replaced by Cl in $CDCl_3$ (Figure 5). In fact the reaction of propargyl chloride **f3** with an alkyne in C_6D_6 did not proceed. The isolated **7a** was not transformed into the minor product in a

solution, suggesting that there is no equilibrium between the two products.[16] The complex **4a** also reacted with alkynes to give **7a**, albeit in low yield.



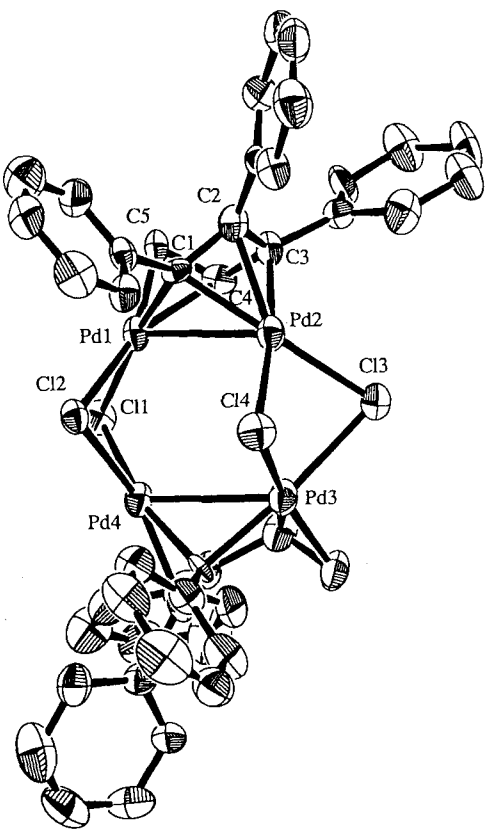


Figure 5. Molecular structure of **7b**. Selected bond distances (Å): Pd1-Cl1 = 2.456(6), Pd1-Cl2 = 2.388(7), Pd2-Cl3 = 2.423(7), Pd2-Cl4 = 2.412(8), Pd2-C1 = 2.10(2), Pd2-C2 = 2.17(3), Pd2-C3 = 2.12(3), Pd1-C1 = 2.03(2), Pd1-C4 = 2.13(2), Pd1-C5 = 2.12(3), C1-C2 = 1.37(2), C2-C3 = 1.34(2). Pd1-Pd2 = 2.888(3). Selected angle (deg): C1-C2-C3 = 110(2), C2-C3-C4 = 113(2), C3-C4-C5 = 121(2).

3-6 Conclusion

I prepared novel type μ-η^3-allenyl/propargyldipalladium complexes. The μ-η^3-allenyl/propargyl group is almost linear and parallels the Pd-Pd bond. These complexes reacted with HCl to give the first example of μ-vinylcarbenedipalladium complex or to undergo hydrogenation of μ-η^3-allenyl/propargyl ligand. In addition, I succeeded in the C-C bond formation reactions of μ-vinylcarbenedipalladium complexes.

3-7 Experimental Section

General Procedures.

Most of commercially available reagents were used without further purification. All reactions and manipulations of air- and moisture-sensitive compounds were carried out under an atmosphere of dry Ar by use of standard vacuum line techniques. ^{1}H NMR , ^{13}C NMR, and ^{31}P NMR spectra were recorded on JEOL JNM-GSX 270 (270 MHz), JEOL JNM-GSX 400 (400 MHz), and Bruker AM600 (600 MHz) spectrometers as solutions in $CDCl_3$ with a reference to $SiMe_4$ (δ 0.00), $CDCl_3$ (δ 77.0) and H_3PO_4 (δ 0.00). IR spectra were recorded on a Hitachi 270-50 infrared spectrophotometer as KBr pellets. Melting points were determined on a Kyoto Keiryoki Seisakujo micro melting point apparatus. Single crystal X-ray structure determinations were carried out on a Rigaku AFC5R diffractometer. Elemental analyses were obtained at the Analytical Center, Faculty of Engineering, Osaka University.

All of the solvents were distilled prior to use. Most commercially available reagents were used without further purification. *trans*-Pd(η^1-$CH_2C{\equiv}CSiMe_3$)(Cl)(PPh_3)$_2$ (**1b**), *trans*-Pd(η^1-$CH_2C{\equiv}CBu^t$)(Cl)(PPh_3)$_2$ (**1 c**), *trans*-Pd(η^1-$CH{=}C{=}CH_2$)(Cl)(PPh_3)$_2$ (**1 d**) were prepared according to the published methods.[8a] The mixture of *trans*-Pd(η^1-C(Ph)=C=CH_2)(Cl)(PPh_3)$_2$ and *trans*-Pd(η^1-$CH_2C{\equiv}CPh$)(Cl)(PPh_3)$_2$ (**1a**) was obtained according to the literature procedure[8a] (see Chapter **1-6**).

Typical Procedure for preparation of (μ-η^3-PhCCCH$_2$)(μ-Cl)Pd$_2$(PPh$_3$)$_2$ (2a).

120.0 mg (0.154 mmol) of **1a** and 124.0 mg (0.120 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$ were dissolved in 3.0 mL of CH_2Cl_2. After 30 min, the reaction mixture was separated by column (silica gel, 100-200 mesh, CH_2Cl_2) and first yellow-orange eluent was concentrated to give **2a** (88.0 mg) in 65% isolated yield. Same reaction was carried out in NMR tube (100% NMR yield, after 20 min). Mp 105-109 °C (dec); IR (KBr) 2190 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.22 (dd, J_{PH} = 4.32, 2.43 Hz, 2H), 6.85 (m, 5H), 7.26 (m, 9H), 7.39 (m, 9H), 7.48 (m, 6H), 7.67 (m, 6H); ^{13}C{^{1}H} NMR δ 9.52 (s, CCH_2), 96.14 (dd, J_{PC} = 5.1, 2.0 Hz, CCH_2), 102.96 (dd, J_{PC} = 10.3, 4.2 Hz, PhCC); ^{31}P{^{1}H} NMR δ 28.81 (d, J_{PP}= 85.6 Hz), 29.41 (d, J_{PP} = 85.6 Hz); Anal. Calcd for $C_{45}H_{37}ClP_2Pd_2$: C, 60.86; H, 4.20. Found C, 60.12; H, 4.22.

Preparation of (μ-η^3-Me$_3$SiCCCH$_2$)(μ-Cl)Pd$_2$(PPh$_3$)$_2$ (2b).

To a solution of 7.0 mg (0.0090 mmol) of **1b** in 0.7 mL of $CDCl_3$ was added 4.7 mg (0.0045 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$ at 25 °C. The reaction was monitored by ^{1}H and ^{31}P NMR. After 20 min, **2b** was yielded (85%). ^{1}H NMR ($CDCl_3$) δ -0.21 (s, 9H), 2.08 (d, J_{PH} = 6.6 Hz, 2H), 7.40 (m, 18H), 7.55 (m, 12H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 7.67 (s, CCH_2), 84.55 (d, J_{PC} = 6.2 Hz, CCH_2), 117.85 (s, Me$_3$SiCC); ^{31}P{^{1}H} NMR δ 24.45 (d, J_{PP}= 101.8 Hz), 27.85 (d, J_{PP} = 101.8 Hz).

Preparation of (μ-η^3-^{t}BuCCCH$_2$)(μ-Cl)Pd$_2$(PPh$_3$)$_2$ (2c).

The procedure was similar to that for **2a, b**. Isolated yield 13% (NMR yield 84%); Mp 135-137 °C (dec); ^{1}H NMR ($CDCl_3$) δ 0.86 (s, 9H), 2.07 (d, J_{PH} = 5.9 Hz, 2H), 7.38 (m, 18H), 7.62 (m, 6H), 7.73 (m, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 10.31 (d, J_{PC} = 3.3 Hz, CCH_2), 93.59 (dd, J_{PC} = 12.3, 2.8 Hz, CCH_2), 111.66 (d, J_{PC} = 4.5 Hz, t-BuCC); ^{31}P{^{1}H} NMR δ 26.05 (d, J_{PP}= 80.4 Hz), 29.72 (d, J_{PP} = 80.4 Hz); Anal. Calcd for $C_{43}H_{41}ClP_2Pd_2(C_6H_6)_{0.5}$: C, 60.91; H, 4.89. Found C, 61.00; H, 5.09.

Preparation of (μ-η^3-HCCCH$_2$)(μ-Cl)Pd$_2$(PPh$_3$)$_2$ (2d).

The procedure was similar to that for **2a, b**. Isolated yield 12% (NMR yield 29%); Mp 129-131 °C (dec); IR (KBr) 2180 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.18 (ddd, J_{HH} = 2.3 Hz, J_{PH} = 6.4, 0.7 Hz, 2H), 5.64 (tdd, J_{HH} = 2.3 Hz, J_{PH} = 32.1, 1.0 Hz, 1H), 7.40(m, 20H), 7.65 (m, 10H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 11.50 (s, CCH_2), 79.23 (t, J_{PC} = 5.7 Hz, CCH_2), 108.49 (d, J_{PC} = 4.9 Hz, HC*C*); ^{31}P{^{1}H} NMR δ 26.70 (d, J_{PP} = 98.2 Hz), 31.29 (d, J_{PP} = 98.2 Hz); Anal. Calcd for $C_{39}H_{33}P_2Pd_2Cl$: C, 57.69; H, 4.10. Found: C, 57.52; H, 4.32.

Typical Procedure for preparation of (μ-η^3-PhCCCH$_2$)(μ-SPh)Pd$_2$(PPh$_3$)$_2$ (2a-SPh).

430.0 mg (0.550 mmol) of **1a**, 342.0 mg (0.330 mmol) of $Pd_2(dba)_3$·$CHCl_3$ and 141.4 mg (1.10 mmol) of NaSPh were dissolved in 20.0 mL of CH_2Cl_2. After 20 min, the reaction mixture was concentrated and purified by column (silica gel, 100-200 mesh, CH_2Cl_2) and first yellow-orange eluent was concentrated to give **2a-SPh** (412.6 mg) in 78% isolated yield. Mp 102 °C (dec); ^{1}H NMR ($CDCl_3$) δ 2.13 (dd, J_{PH} = 5.4, 2.2 Hz, 2H), 6.65 (t, J_{PH} = 7.3 Hz, 2H), 6.82 (m, 8H), 7.13 (m, 6H), 7.31 (m, 18H), 7.54 (m, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 8.30 (s, CCH_2), 98.81 (d J_{PC} = 6.6 Hz, CCH_2), 109.77 (dd, J_{PC} = 8.3, 2.7 Hz, HC*C*); ^{31}P{^{1}H} NMR δ 30.26 (d, J_{PP}= 92.8 Hz), 31.07 (d, J_{PP} = 92.8 Hz); Anal. Calcd for $C_{51}H_{42}ClP_2Pd_2S$: C, 63.69; H, 4.40; S, 3.33. Found C, 63.67; H, 4.70; S, 3.40.

Preparation of (μ-η^3-PhCCCH$_2$)(μ-I)Pd$_2$(PPh$_3$)$_2$ (2a-I).

The procedure was similar to that for **2a-SPh**. Yield 63%; ^{1}H NMR ($CDCl_3$) δ 2.55 (dd, J_{PH} = 4.6, 1.9 Hz, 2H), 7.16 (m, 5H), 7.26 (m, 9H), 7.40 (m, 9H), 7.51 (m, 6H), 7.68 (m, 6H); ^{31}P{^{1}H} NMR δ 37.08 (d, J_{PP}= 94.6 Hz), 37.65 (d, J_{PP} = 94.6 Hz); Anal. Calcd for $C_{45}H_{37}IP_2Pd_2$: C, 55.18; H, 3.81. Found C, 55.03; H, 3.96.

Other Procedure for preparation of 2a.

To a solution of 1.5 mg (0.010 mmol) of **3a** in 0.7 mL of $CDCl_3$ were added 10.3 mg

(0.010 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$ and 5.2 mg (0.020 mmol) of PPh_3 at 25 °C. The reaction was monitored by ^1H and ^{31}P NMR. After 30 min, **2a** was yielded (100%). Similar reaction was carried out for **3c**. After 30 min, **2c** was yielded (75%).

Reaction of 2a with HCl.

To a solution of 29.9 mg (0.0337 mmol) of **2a** in 0.5 mL of CH_2Cl_2 were added 0.1 mL of H_2O and 4.6 mg (0.042 mmol) of $(CH_3)_3SiCl$ at room temperature. The mixture changed to yellow suspension within 10 min. After 45 min, addition of 0.35 mL of hexane to the suspension yielded yellow solids of **(μ-η^3-Cl(PPh$_3$)Pd(Ph)CCHCH$_2$)Pd(μ-Cl)(PPh$_3$) (4a)** (24.4 mg, 78%). Same reaction was carried out in NMR tube (89% NMR yield, after 30 min). ^1H NMR spectra of **4a** showed the presence of two isomers which I tentatively assume to arise from different disposition of P2 and Cl2 on Pd2 (see Fig. 3). Spectral data for **4a** (major : minor = 67 : 33): major isomer ^1H NMR ($CDCl_3$) δ 3.28 (dd, J_{HH} = 7.5 Hz, J_{PH} = 1.2 Hz, 1H), 3.62 (d, J_{HH} = 10.7 Hz, 1H), 5.31 (ddd, J_{HH} = 7.5, 10.7 Hz, J_{PH} = 6.3 Hz, 1H); $^{31}P\{^1H\}$ NMR δ 28.65 (d, J_{PP} = 4.2 Hz), 32.85 (d, J_{PP} = 4.2 Hz). minor isomer ^1H NMR ($CDCl_3$) δ 2.58 (dd, J_{HH} = 13.0 Hz, J_{PH} = 1.6 Hz, 1H), 3.04 (dd, J_{HH} = 6.7 Hz, J_{PH} = 1.0 Hz, 1H), 5.52 (ddd, J_{HH} = 13.0, 6.7 Hz, J_{PH} = 3.4 Hz, 1H); $^{31}P\{^1H\}$ NMR δ 25.15 (brs), 20.55 (brs); Anal. Calcd for $C_{45}H_{38}Cl_2P_2Pd_2 \cdot (CH_2Cl_2)_{1.5}$ C, 53.10; H, 3.93. Found: C, 53.03; H, 4.02.

Reaction of 2a-I with HCl.

The procedure was similar to that for **2a**. Yellow solids of **(μ-η^3-Cl(PPh$_3$)Pd(Ph)CCHCH$_2$)Pd(μ-I)(PPh$_3$) (4a-I)** were obtained. Yield 76% (NMR yield 76%); ^1H NMR ($CDCl_3$) δ 3.47 (d, J_{HH} = 12.0 Hz, 1H), 3.85 (d, J_{HH} = 6.8 Hz, 1H), 5.18 (ddd, J_{HH} = 12.0, 6.8 Hz, J_{PH} = 6.2 Hz, 1H), 7.16 (m, 3H), 7.26 (m, 4H), 7.47 (m, 13H), 7.65 (m, 13H), 7.88 (d, J_{HH} = 9.4 Hz, 2H); $^{31}P\{^1H\}$ NMR δ 28.33 (s), 30.28 (s); Anal. Calcd for $C_{45}H_{38}ClIP_2Pd_2$: C, 53.20; H, 3.77. Found: C, 52.48; H, 4.04.

Reaction of 2a with CH_3COCl.

To a solution of 92.2 mg (0.104 mmol) of **2a** in 1.5 mL of CH_2Cl_2 was added 12.2 mg (0.155 mmol) of CH_3COCl at room temperature. After 1 h, the reaction mixture was filtered and the filtrate was concentrated under reduced pressure in a rotary evaporator. Then, the red solid was purified by column (silica gel, 100-200 mesh, CH_2Cl_2 and CH_2Cl_2/ethyl acetate (10:1)), and recrystallization from CH_2Cl_2-hexane gave yellow solids of **(μ-η^3-Cl(PPh$_3$)Pd(Ph)CC(COCH$_3$)CH$_2$)Pd(μ-Cl)(PPh$_3$) (5)** (20.7 mg, 21%). ^{1}H NMR ($CDCl_3$) δ 2.70 (s, 1H), 3.30 (s, 3H), 3.37 (s, 1H); $^{31}P\{^1H\}$ NMR δ 27.24 (s), 28.53 (s).; Anal. Calcd for $C_{47}H_{40}Cl_2OP_2Pd_2$ C, 58.41; H, 4.17. Found: C, 58.14; H, 4.20.

Reaction of 2a-SPh with 2 HCl.

To a solution of 11.0 mg (0.0114 mmol) of **2a-SPh** in 0.7 mL of $CDCl_3$ were added 0.03 mL of H_2O and 2.5 mg (0.0230 mmol) of $(CH_3)_3SiCl$ at 0 °C. The reaction was monitored by ^{1}H and ^{31}P NMR. After 5 min, Pd(η^3-$CH_2CHCHPh$)Cl(PPh_3) was yielded (69%).

Reaction of 4a with $PhSnBu_3$.

To a solution of 10.7 mg (0.0116 mmol) of **4a** in 0.7 mL of $CDCl_3$ was added 5.1 mg (0.012 mmol) of Ph_4Sn at 40 °C. The reaction was monitored by ^{1}H and ^{31}P NMR. After 45 h, **Pd(η^3-CH$_2$CHC(Ph)$_2$)(Cl)(PPh$_3$) (5)** was yielded (69%). ^{1}H NMR ($CDCl_3$) δ 2.76 (dd, J_{HH} = 7.3, 2.2 Hz, 1H), 2.92 (dd, J_{HH} = 12.5, 2.2 Hz, 1H), 5.83 (dd, J_{HH} = 12.5, 7.3 Hz, 1H), 7.31-7.70 (m, 25H); $^{31}P\{^1H\}$ NMR δ 28.25 (s).

Preparation of (μ-OH)(μ-Cl)Pd$_2$(PPh$_3$)$_2$(μ-η^1:η^3-CH$_2$CCPh)$_2$(μ-Cl)$_2$Pd$_2$ (6).

40.0 mg (0.0433 mmol) of **4a** and 4.5 mg (0.0044 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$ were dissolved in 1.5 mL of CH_2Cl_2 under air. After 62 h, the reaction mixture was filtered and the filtrate was concentrated under reduced pressure in a rotary evaporator. Then, the dark-green solids were recrystallized from CH_2Cl_2-hexane to give orange crystals of **6** (17.0 mg, 60%). Same reaction was carried out in NMR tube (91%, 71 h). ^{1}H NMR

($CDCl_3$) δ 2.17 (t, J_{HP} = 2.0 Hz, 1H), 3.73 (d, J_{HH} = 6.6 Hz, 2H), 4.37 (d, J_{HH} = 11.4 Hz, 2H), 4.66 (ddd, J_{HH} = 6.6, 11.4 Hz, J_{PH} = 5.0 Hz, 1H), 7.02 -7.81 (m, 40H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 57.68 (s, CH_2C), 112.68 (d, J_{PC} = 9.3 Hz, CH_2C), 122.83 (s, *C*Ph); $^{31}P\{^1H\}$ NMR δ 31.63 (s); Anal. Calcd for $C_{54}H_{47}Cl_3OP_2Pd_4$: C, 49.66; H, 3.63. Found C, 49.44; H, 3.82.

Reaction of 6 with HCl and PPh_3.

To a solution of 2.9 mg (0.0022 mmol) of **6** in 0.7 mL of $CDCl_3$ were added 0.3 mg (0.0028 mmol) of $(CH_3)_3SiCl$ and 1.2 mg (0.0046 mmol) of PPh_3 at 25 °C. The reaction was monitored by ^1H and ^{31}P NMR. After 5 min, **4a** was yielded (99%).

Reaction of 6 with $CH_3C{\equiv}CCH_3$.

To a $CDCl_3$ solution (0.7 mL) of 121 mg (0.0930 mmol) of **6** was added 11.0 mg (0.203 mmol) of $CH_3C{\equiv}CCH_3$ in an NMR tube. The NMR tube was shielded and heated at 60 °C. The reaction was monitored by ^1H NMR. After 17 h, **[(μ-Cl)Pd(μ-Cl)Pd(μ-η^1:η^3:η^2-$CH_3CC(CH_3)C(Ph)CH{=}CH_2$)]$_2$ (7a)** (major) and a minor product were yielded (NMR yield 76%, major:minor = 67:33). Then, the reaction mixture was purified by column (silica gel, 100-200 mesh, CH_2Cl_2 and ethyl acetate/hexane (1:1)), and recrystallization from CH_2Cl_2-hexane gave orange crystals of **7a** (36.7 mg, isolated 43%). Major: ^1H NMR ($CDCl_3$) δ 2.05 (s, 6H), 2.10 (s, 6H), 4.19 (dd, J_{HH} = 13.2, 1.6 Hz, 2H), 4.83 (dd, J_{HH} = 7.2, 1.6 Hz, 2H), 6.03 (dd, J_{HH} = 13.2, 7.2 Hz, 2H), 7.2-7.8 (m, 10H); Minor: ^1H NMR ($CDCl_3$) δ 2.01 (s, 6H), 2.09 (s, 6H), 4.15 (dd, J_{HH} = 12.8, 1.6 Hz, 2H), 4.73 (dd, J_{HH} = 7.2, 1.6 Hz, 2H), 6.09 (dd, J_{HH} = 12.8, 7.2 Hz, 2H), 7.2-7.8 (m, 10H); Anal. Calcd for $C_{26}H_{28}Cl_4Pd_4$: C, 34.39; H, 3.11. Found C, 34.46; H, 3.09.

Reaction of 6 with PhC≡CPh.

The procedure was similar to that for $CH_3C{\equiv}CCH_3$. **[(μ-Cl)Pd(μ-Cl)Pd(μ-η^1:η^3:η^2-$PhCC(Ph)C(Ph)CH{=}CH_2$)]$_2$ (7b)** (major) and a minor product were obtained (NMR yield 77%, major:minor = 68:32). Then, the reaction mixture was purified by

column (silica gel, 100-200 mesh, CH_2Cl_2 and ethyl acetate/hexane (1:1)), and recrystallization from CH_2Cl_2-hexane gave orange crystals of **7b** (isolated 48%). Major: ^1H NMR ($CDCl_3$) δ 4.68 (dd, J_{HH} = 13.2, 1.6 Hz, 2H), 5.09 (dd, J_{HH} = 7.3, 1.6 Hz, 2H), 6.47 (dd, J_{HH} = 13.2, 7.3 Hz, 2H), 6.80-7.50 (m, 60H); Minor: ^1H NMR ($CDCl_3$) δ 4.57 (dd, J_{HH} = 13.2, 1.6 Hz, 2H), 4.94 (dd, J_{HH} = 7.3, 1.6 Hz, 2H), 6.54 (dd, J_{HH} = 13.2, 7.3 Hz, 2H), 6.80-7.50 (m, 60H); Anal. Calcd for $C_{46}H_{36}Cl_4Pd_4 \cdot CH_2Cl_2$: C, 45.48; H, 3.09. Found C, 45.40; H, 3.05.

Single crystal X-ray diffraction study.

All data were obtained on a Rigaku AFC-5R diffractometer with graphite-monochromated Mo-Kα radiation. All calculations were carried out with the TEXSAN crystallographic software package of Molecular Structure Corporation. The structure was solved by the direct method and refined by the full-matrix least-squares procedure, the function minimized being $\Sigma w(|F_o|-|F_c|)^2$. The non-hydrogen atoms were refined anisotropically. All the positions of the hydrogen atoms were calculated by stereochemical considerations.

(μ-η^3-HCCCH$_2$)(μ-Cl)Pd$_2$(PPh$_3$)$_2$ (2d·THF)

A yellow crystal (0.25 × 0.25 × 0.40 mm) was obtained from THF/hexane at -30 °C and was mounted on a glass fiber with epoxy resin. $C_{43}H_{41}ClOP_2Pd_2$, M = 884.04, triclinic, space group *P*1*(#1)*, a = 10.090(2) Å, b = 11.768(2) Å, c = 8.747(1) Å, α = 94.16(1)°, β = 108.35(1)°, γ = 78.19(1)°, *V* = 964.9(3) Å^3, *Z* = 1, *D*calc = 1.521 g/cm^3, *F*(000) = 446.00, μ(Mo-Kα) = 11.17 cm^{-1} by least squares refinement on diffractometer angles from automatically centered reflections, 2θ range 27.1-27.5°, λ = 0.71069 Å. The final *R* and R_w values were 0.056 and 0.045, respectively, for 3435 reflections (I > 3.00σ(I)).

(μ-η^3-PhCCCH$_2$)(μ-SPh)Pd$_2$(PPh$_3$)$_2$ (2a-SPh)

A yellow crystal (0.40 × 0.40 × 0.50 mm) was obtained from CH_2Cl_2/hexane at -30 °C and was mounted on a glass fiber with epoxy resin. $C_{51}H_{42}P_2Pd_2S$, M = 961.70 monoclinic, space group $P2_1/n$(#14); a = 16.809(2) Å, b = 16.608(3) Å, c = 17.238(2) Å, β = 114.871(8)°, V = 4365(1) Å^3, Z = 4, D_{calc} = 1.463 g/cm^3, F(000) = 1944.00, μ(Mo-Kα) = 9.64 cm^{-1} by least squares refinement on diffractometer angles from automatically centered reflections, 2θ range 27.3-27.5°, λ = 0.71069 Å. The final R and R_w values were 0.036 and 0.029, respectively, for 7988 reflections (I > 3.00σ(I)).

μ-η^1:η^3-(PhCCHCH$_2$)PdCl(PPh$_3$)Pd(μ-Cl)(PPh$_3$) (4a·(H$_2$O)$_3$)

A yellow crystal (0.30 × 0.30 × 0.30 mm) was obtained from CH_2Cl_2/hexane at -30 °C and was mounted on a glass fiber with epoxy resin. $C_{45}H_{44}Cl_2O_3P_2Pd_2$, M = 978.49 triclinic, space group $P\bar{1}$(#2); a = 10.233(2) Å, b = 24.617(7) Å, c = 9.028(2) Å, α = 97.69(2)°, β = 108.69(1)°, γ = 87.23(2)°, V = 2134.8(8) Å^3, Z = 2, D_{calc} = 1.463 g/cm^3, F(000) = 988.00, μ(Mo-Kα) = 10.81 cm^{-1} by least squares refinement on diffractometer angles from automatically centered reflections, 2θ range 27.4-27.5°, λ = 0.71069 Å. The final R and R_w values were 0.065 and 0.082, respectively, for 7988 reflections (I > 3.00σ(I)).

(μ-OH)(μ-Cl)Pd$_2$(PPh$_3$)$_2$(μ-η^1:η^3-CH$_2$CCPh)$_2$(μ-Cl)$_2$Pd$_2$ (6·(H$_2$O)$_4$·CHCl$_3$)

A yellow crystal (0.30 × 0.30 × 0.40 mm) was obtained from $CHCl_3$/hexane at -30 °C and was mounted on a glass fiber with epoxy resin. $C_{55}H_{52}Cl_6O_5P_2Pd_4$, M = 1493.28 triclinic, space group $P\bar{1}$(#2); a = 15.276(5) Å, b = 16.798(4) Å, c = 15.080(4) Å, α = 112.20(2)°, β = 119.30(2)°, γ = 68.64(2)°, V = 3046(1) Å^3, Z = 2, D_{calc} = 1.628 g/cm^3, F(000) = 1476.00, μ(Mo-Kα) = 15.21 cm^{-1} by least squares refinement on diffractometer angles from automatically centered reflections, 2θ range 27.4-27.5°, λ = 0.71069 Å. The final R and R_w values were 0.083 and 0.119, respectively, for 8758 reflections (I > 3.00σ(I)).

[(μ-Cl)Pd(μ-Cl)Pd(μ-η^1:η^3:η^2-PhCC(Ph)C(Ph)CH=CH$_2$)]$_2$ (7b·$CH_3COOC_2H_5$·C_6H_{14})

An orange crystal (0.20 × 0.20 × 0.20 mm) was obtained from ethyl acetate/hexane at -30 °C and was mounted on a glass fiber with epoxy resin. $C_{56}H_{58}Cl_4O_2Pd_4$, M = 1330.48 monoclinic, space group $P2_1/c$(#14); a = 12.111(8) Å, b = 16.15(1) Å, c = 27.182(10) Å, β = 98.48(5)°, V = 5258(4) Å^3, Z = 4, D_{calc} = 1.681 g/cm^3, F(000) = 2648.00, μ(Mo-Kα) = 15.90 cm^{-1} by least squares refinement on diffractometer angles from automatically centered reflections, 2θ range 5.3-15.7°, λ = 0.71069 Å. The final R and R_w values were 0.058 and 0.060, respectively, for 2574 reflections (I > 3.00σ(I)).

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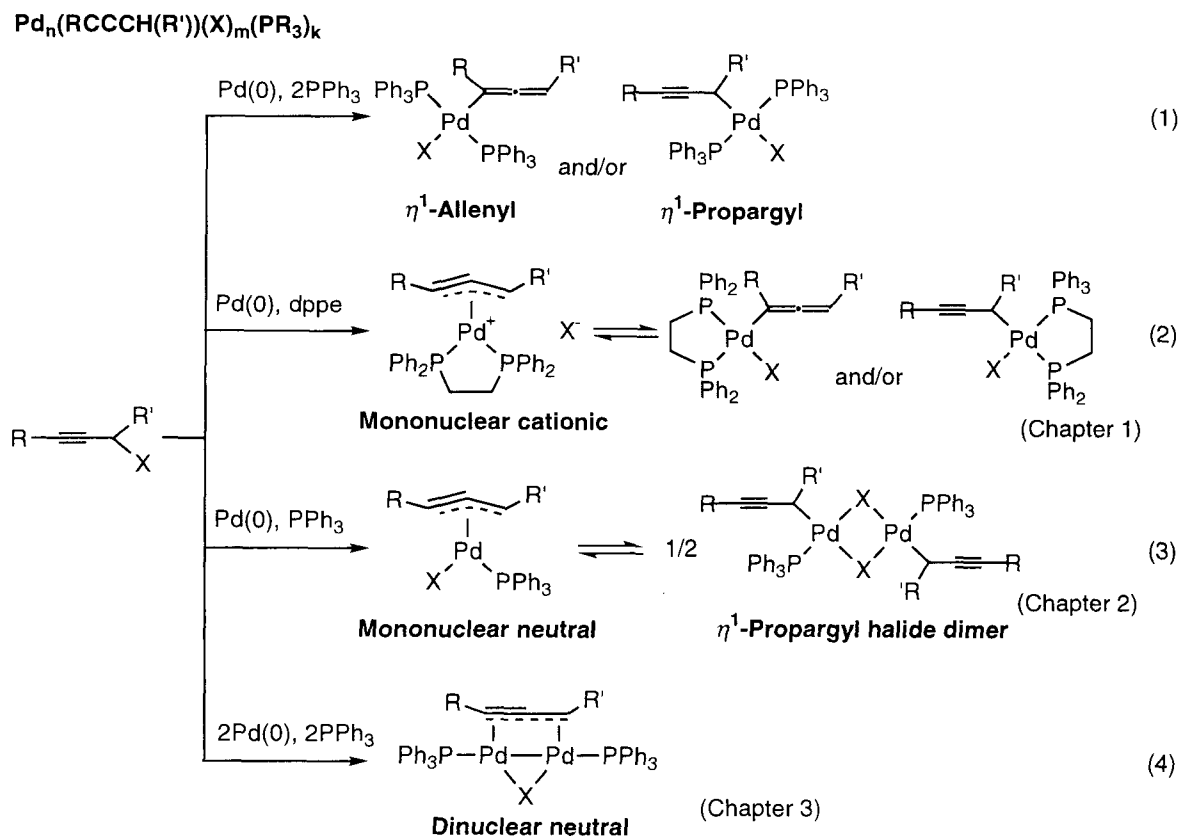
(19) μ-Carbene complexes react with alkynes to give μ-η^3-vinylcarbene complexes: see ref. 13.

Conclusion

I prepared novel three types palladium complexes containing η^3-allenyl/propargyl ligand. The coordination mode of allenyl and propargyl species on palladium in $Pd_n(Propargyl)(X)_m(PR_3)_k$ is controlled by appropriate choice of the following factors: (i) the ratio of propargyl halide, phosphine ligand and Pd(0) complex in the course of oxidative addition to form allenyl/propargyl palladium complexes, (ii) substituents of propargyl ligand, (iii) halide X on Pd, (iv) phosphine ligands (v) solvents, (vi) temperature.



η^1-Allenyl and η^1-propargyl mononuclear palladium complexes were obtained by the reaction of propargyl halide with 1 equiv of Pd(0) and 2 equiv of PPh_3 (eq. 1). When phosphine ligand was dppe and R' was Me, cationic η^3-allenyl/propargylpalladium complexes were directly observed as an equilibrium isomer together with neutral η^1-type complexes (eq. 2). The treatment of propargyl halide with 1 equiv of $Pd(PPh_3)$ afforded the equilibrium mixture of neutral η^3-allenyl/propargylpalladium and η^1-propargyl halide

dimer (eq. 3). Finally the treatment of propargyl halides with 2 equiv of $Pd(PPh_3)$ afforded neutral μ-η^3-allenyl/propargyldipalladium complexes (eq. 4).

Each type complex exhibited specific reactivity. Mononuclear cationic η^3-allenyl/propargylpalladiums are very prone to undergo nucleophilic attack at the central carbon of η^3-allenyl/propargyl ligand. Neutral η^3-allenyl/propargylpalladiums are more susceptible toward organometallic reagents, such as organotin than other type mononuclear complexes. These complexes are the more reactive intermediate in the homogeneous catalytic reactions. Dinuclear neutral η^3-allenyl/propargylpalladium complexes are susceptible to the attack of an electrophile at the central carbon, yielding μ-vinylcarbene dipalladium complexes.

The present systematic and fundamental data might be useful in gaining insight into various mono and polynuclear metals bearing unsaturated hydrocarbon ligands, and become some guides for the application of the related organometallics in the synthetic, materials, and biological chemistry.

List of Publications

The contents of this thesis are composed of the following papers.

(1) Synthesis and Structure of Cationic η^3-Allenyl/propargylpalladium Complexes
Sensuke Ogoshi, Ken Tsutsumi, Hideo Kurosawa
J. Organomet. Chem., **1995**, *493*, C19.

(2) Synthesis, Structure and Reactivity of η^3-Allenyl/Propargyl Dinuclear Palladium Complexes
Sensuke Ogoshi, Ken Tsutsumi, Motohiro Ooi, Hideo Kurosawa
J. Am. Chem. Soc., **1995**, *117*, 10415.

(3) Synthesis, Structure, and Reactivity of Neutral η^3-Propargylpalladium Complexes
Ken Tsutsumi, Sensuke Ogoshi, Shinji Nishiguchi, Hideo Kurosawa
J. Am. Chem. Soc., **1998**, *120*, 1938.

(4) Carbon-carbon Bond Forming Reactions of μ-Vinylcarbenedipalladium Complexes
Sensuke Ogoshi, Ken Tsutsumi, Tsutomu Shinagawa,
Kiyomi Kakiuchi, Hideo Kurosawa
Chem. Lett., **1999**, 123.

(5) Cross-coupling Reactions Proceeding through η^1- and η^3-Propargyl/allenyl-palladium(II) intermediates
Ken Tsutsumi, Sensuke Ogoshi, Kiyomi Kakiuchi, Shinji Nishiguchi,
Hideo Kurosawa
Inorg. Chim. Acta, in press.

(6) Synthesis and Characterization of Some Cationic η^3-Propargylpalladium Complexes
Ken Tsutsumi, Tomohiro Kawase, Kiyomi Kakiuchi,
Sensuke Ogoshi, Yuji Okada, Hideo Kurosawa
Bull. Chem. Soc. Jpn., in press.

Supplementary List of Publications

(1) Palladium-Catalyzed Reductive Homocoupling Reaction of 3-Silylpropargyl Carbonates. New Entry into Allene-Yne Compounds

Sensuke Ogoshi, Shinji Nishiguchi, Ken Tsutsumi, Hideo Kurosawa

J. Org. Chem., **1995**, *60*, 4650.

(2) Mutual Isomerization of η^1-Allenyl and η^1-Propargyl Complexes of Platinum via a Five- coordinate η^3-Allenyl/propargyl Intermediate

Sensuke Ogoshi, Yoshiaki Fukunishi, Ken Tsutsumi, Hideo Kurosawa

J. Chem. Soc., Chem. Commun., **1995**, 2485.

(3) Mechanistic Studies on Mutual Isomerization of Propargyl- and Allenylplatinum(II) Complexes

Sensuke Ogoshi, Yoshiaki Fukunishi, Ken Tsutsumi, Hideo Kurosawa

Inorg. Chim. Acta, **1997**, *265*, 9.

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