STUDIES ON THE NEW SYNTHETIC AND REACTIVITY ASPECTS OF π-ALLYL PALLADIUM COMPLEXES

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OSAKA UNIVERSITY

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(π-アリルパラジウム錯体の新しい合成法と反応性に関する研究)

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Preface

This work was preformed under the guidance of Professor Shinji Murai at Department of Applied Fine Chemistry, Faculty and Engineering, Osaka University.

I would like to express my deepest gratitude to Professor Shinji Murai for his guidance, insight, compassion, and inspiration throughout my career as a graduate student. A true teacher he is, to a great extent, responsible for my progress as a chemist. I will always be indebted to him for this.

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Sensuke Ogoshi

List of publications

(1) Novel Decarbonylation of a Formal Homoacyl-Palladium Linkage, $PdCH(CR{=}CH_2)C(O)SiR'_3$, Affording a $PdCH(CR{=}CH_2)SiR'_3$ Moiety
Ogoshi, S.; Ohe, K.; Chatani, N.; Kurosawa, H.; Kawasaki, Y.; Murai, S.
Organometallics **1990**, *9*, 3021

(2) Reaction of 1-Silyl Dienol Silyl Ethers with Palladium(II) Complexes: Novel Formation of Sevral Types of (η^3-allyl)palladium(II) Complexes via the Versatile Complex [η^3-1-(Silylcarbonyl)allyl]-palladium Chloride
Ogoshi, S.; Ohe, K.; Chatani, N.; Kurosawa, H.; Murai, S.
Organometallics **1992**, *10*, 3813.

(3) Convenient synthesis of [η^3-1-(formyl)allyl]- and [η^3-1-(dimethoxymethyl)allyl]palladium chlorides
Ogoshi, S; Hirako, K.; Nakanishi, J.; Ohe, K.; Murai, S.
J. Organomet. Chem., in press.

(4) Palladium-Catalyzed Reactions of Ketone α-Carbonates with Norbornenes. An Unusual Cyclopropanation
Ogoshi, S.; Morimoto, T.; Nishio, K.; Ohe, K.; Murai, S.
J. Org. Chem., in press.

(5) Reaction of Palladium(II) Complexes with Allylsilanes: Convenient Synthesis of [η^3-1-(Silyl)allyl]palladium Complexes
Ogoshi, S.; Yoshida, W.; Ohe, K.; Murai, S.
Organometallics, in press.

Supplementary List of Publications

(1) Novel Dependency of Stereochemistry upon Metal, Ligand, and Solvent in Oxidative Addition of Allylic Chloride to Pd(0) and Pt(0) Complexes
Kurosawa, H.; Ogoshi, S.; Kawasaki, Y.; Murai, S.; Miyoshi, M.; Ikeda, I.
J. Am. Chem. Soc. **1990**, *112*, 2813.

(2) Allyl Group Transfer between M(II) and M(0) Centers (M = Pd, Pt) Proceeding through *Anti* Nucleophilic Attack at η^3-Allyl Ligand
Kurosawa, H.; Ogoshi, S.; Kawasaki, Y.; Chatani, N.; Murai, S.; Ikeda, I.
Chem. Lett. **1990**, 1745.

(3) Novel Syn Oxidative Addition of Allylic Halides with Olefin Complexes of Pd(0) and Pt(0)
Kurosawa, H.; Kajimaru, H.; Ogoshi, S.; Yoneda, H.; Miki, K.; Kasai, N.;Murai, S.; Ikeda, I.
J. Am. Chem. Soc. **1992**, *114*, 8417.

(4) Palladium-Catalyzed Reaction of 5-Methylene-1,3-dioxolan-2-ones. A New Access to and Reactivity of Oxatrimethylenemethane-Palladium
Ohe, K.; Matsuda, H.; Ishihara, T.; Ogoshi, S.; Chatani, N.; Murai, S.
J. Org. Chem., in press.

Contents

General Introduction

Recently the chemistry of organotransition-metal complexes has experienced explosive growth in novel substances, new reactions, surprising mechanisms, and further applications to both organic synthesis and industrial processes. Palladium is one of the more versatile transition metals in organometallic chemistry. As a result, (η^3-allyl)palladium complexes have been well investigated.[1] Two distinct types of (η^3-allyl)palladium systems are important: neutral stoichiometric complexes such as the chloride dimer derived from alkenes,[2] and cationic intermediates which arise in catalytic cycles by oxidative addition of allylic substrates to Pd(0) species.[3] Both types of (η^3-allyl)palladium complexes react with nucleophiles to give allylated products under suitable conditions. An application of (η^3-allyl)palladium complexes to organic synthesis has been developed and exploited. This new (η^3-allyl)palladium chemistry can be classified into some reaction types. Thus, the discovery of new reactions which do not belong to known reaction types, may involve new aspects of (η^3-allyl)palladium chemistry.

In this thesis, new aspects of the synthetic utility and the reactivity of (η^3-allyl)palladium complexes have been studied.

Chapter 1 deals with the reaction of palladium(II) complexes with allyl silanes to give [η^3-1-(silyl)allyl]palladium chlorides.

Chapter 2 deals with convenient synthesis of [η^3-1-(formyl)allyl]- and [η^3-1-(dimethoxymethyl)allyl]-palladium chloride.

Chapter 3 deals with the reaction of 1-silyl-dienol silyl ethers with palladium(II) complexes leading to formation of several types of (η^3-allyl)palladium(II) complexes via the versatile [η^3-1-(silylcarbonyl)allyl]-palladium chloride complex.

Chapter 4 deals with palladium-catalyzed reactions of ketone α-carbonates with norbornenes which undergo an unusual cyclopropanation.

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Chapter 1

Reaction of Palladium(II) Complexes with Allylsilanes. Convenient Synthesis of [η^3-1-(Silyl)allyl]palladium Complexes

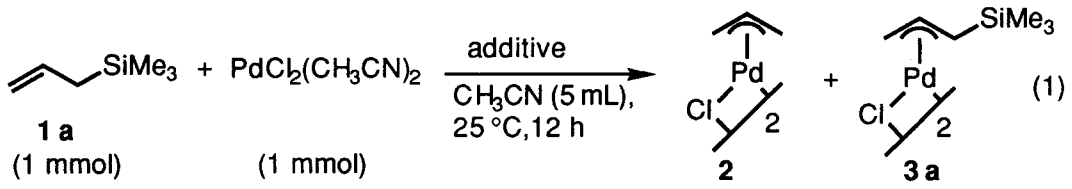
1-1 Introduction

The great diversity of the chemistry of η^3-allyl transition metal complexes has been reported. In particular, (η^3-allyl)palladium chemistry has been well investigated, and its application to organic synthesis has been developed and exploited.[1] The early definitive studies of allyl palladium complexes concerned the preparation of dimeric palladium chloride complexes. (η^3-Allyl)palladium derivatives are readily available from alkenes by reactions with Pd(II) complexes like $PdCl_2$, Na_2PdCl_4 and $Pd(OAc)_2$ under appropriate conditions via deprotonation.[2] Analogously, reaction of $PdCl_2(PhCN)_2$ with olefins containing electron-withdrawing β-substitutents, in particular carbonyl, formed (η^3-allyl)palladium complex under mild conditions.[3] If deprotonation occurred in the reaction of allylsilane with Pd(II) salts, [η^3-(1-silyl)allyl]palladium complexes[4] might be obtained. However, the reaction of palladium(II) salt with allylsilane usually affords (η^3-allyl)palladium derivatives by desilylation under mild conditions.[4,5] I wish to report here selective synthesis

of [η^3-(1-silyl)allyl]palladium chloride by the reaction of palladium(II) salts with allylsilanes. The new reaction does not involve usual desilylation.

1-2 Results and Discussion

The reaction of allyltrimethylsilane (**1a**) with $PdCl_2(CH_3CN)_2$ in CH_3CN at 25 °C afforded anticipated (η^3-allyl)palladium chloride **2** in high yield (91%), an electrophilic reaction of Pd(II) with the double bond assisted by nucleophilic attack of a chloride ion on the silicon atom.[5] Seeking a mild process for deprotonation in this combination, the same reaction was examined in the presence of some additives, amines or Li_2CO_3, and triethylamine was found to be effective for the desired reaction to give [η^3-(1-trimethylsilyl)allyl]palladium chloride (**3a**) (41% yield) with **2** (7% yield) (eq 1). Note that the labile cationic leaving group, trimethylsilyl group, was left intact. Addition of Li_2CO_3 led to exclusive formation of **2**. Other amines were not effective; DBU, TMEDA, and pyridine gave insoluble amine complexes, and immidazole gave palladium black. Furthermore, when the method of Ketley and Braatz using $NaHCO_3$ as an additive[6] was applied to this reaction, only small amounts of **2** and **3a** were obtained (12 and 10% yields, respectively).



1 a (1 mmol) (1 mmol) **2** **3 a** (1)

additive	yield,[a] %	
	2	**3a**
none	91	–
Et_3N (1 mmol)	7	41
Li_2CO_3 (2 mmol)	33	–

[a] NMR yield based on $PdCl_2(CH_3CN)_2$ used

The effect of the amounts of amine and allylsilane was investigated to optimize the reaction conditions and the results are summarized in Table I.

Table I. Effect of the Amounts of Allylsilane and Et_3N in eq 1

allylsilane, mmol	Et_3N, mmol	yield,[a] %	
		2	**3a**[b]
1	1	7	41
	3	0	40
2	3	2	71
3	1	15	74
	2	6	81
	3	0	80
5	3	0	82 (82)[c]

[a] All yields refer to NMR yield based on the $PdCl_2(CH_3CN)_2$ used. [b] **3a** was obtained as a mixture of *syn* and *anti* isomers (uniformly 75/25).
[c] Isolated yield.

The use of more than three equivalents of Et_3N with respect to $PdCl_2(CH_3CN)_2$ was required to suppress the formation of **2** and the use of more than three equivalents of allylsilane was required to afford **3a** in a high yield. Thus, the reaction of three equivalents of allylsilane with $PdCl_2(CH_3CN)_2$ in the presence of three equivalents of Et_3N gave **3a** as the sole product (80% yield based on the Pd used).

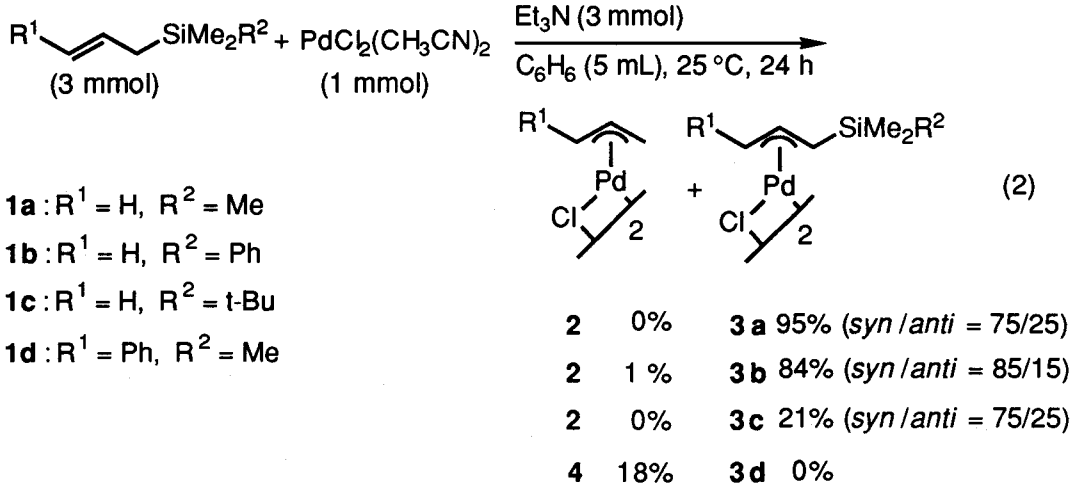
As can be seen in Table II, the use of THF and CH_2Cl_2 as the solvent led to the formation of the desilylated product **2**. Benzene, CH_3CN, and toluene were solvents of choice for the deprotonation. In particular, the reaction of **1a** with $PdCl_2(CH_3CN)_2$ in benzene at 25 °C gave **3a** exclusively in an excellent yield (95%).

Table II. Effect of Solvent on the Yield of **3a** in eq 1

solvent	yield,[a] %	
	2	**3a**
CH_3CN	0	80
THF	5	27
CH_2Cl_2	4	45
C_6H_6	0	78 (95)[b]
toluene	trace	(78)[b]

Reaction conditions: **1a** (3 mmol), $PdCl_2(CH_3CN)_2$ (1 mmol), Et_3N (3 mmol), solvent (5 mL), 25 °C, 12 h
[a]NMR yield based on $PdCl_2(CH_3CN)_2$ used. [b]24 h

The reaction of other allylsilanes with $PdCl_2(CH_3CN)_2$ was examined(eq 2).

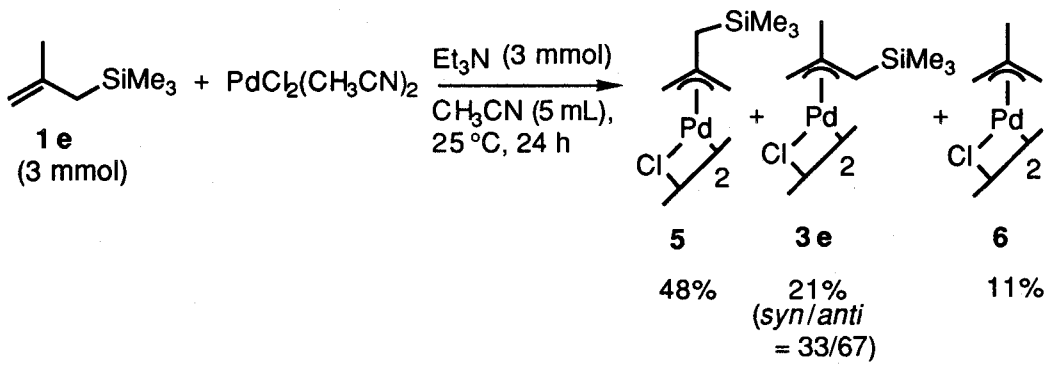


(2)

1a : R^1 = H, R^2 = Me
1b : R^1 = H, R^2 = Ph
1c : R^1 = H, R^2 = t-Bu
1d : R^1 = Ph, R^2 = Me

2	0%	**3a** 95% (*syn*/*anti* = 75/25)
2	1 %	**3b** 84% (*syn*/*anti* = 85/15)
2	0%	**3c** 21% (*syn*/*anti* = 75/25)
4	18%	**3d** 0%

Allyldimethylphenylsilane (**1b**) reacted with $PdCl_2(CH_3CN)_2$ to give [η^3-(1-dimethylphenylsilyl)allyl]-palladium chloride **3b** in a high yield (84%) with small amount of **2** (1%). Allyl-*t*-butyldimethylsilane (**1c**) also reacted with $PdCl_2(CH_3CN)_2$ to afford [η^3-(1-*t*-butyldimethylsilyl)allyl]palladium chloride **3c** (21% yield) exclusively. However, desilylation occurred in the reaction of cinnamyltrimethylsilane (**1d**) to give [η^3-(1-phenyl)allyl]palladium chloride **4** (18% yield) and no deprotonation product. The reaction of 2-methyl-3-(trimethylsilyl)propene (**1e**) with $PdCl_2(CH_3CN)_2$ afforded a mixture of deprotonation products [η^3-(2-methyl-1-trimethylsilyl)allyl]palladium chloride **3e** (21% yield) and [η^3-(2-trimethylsilylmethyl)allyl]palladium chloride (**5**) (48% yield) and a desilylation product [η^3-(2-methyl)allyl]palladium chloride **6** (11% yield) (eq 3).



(3)

A plausible mechanism is described below, but it is only speculative at this time. The desilylation give (η^3-allyl)palladium chloride.[5] Although not clear, a possible role of Et_3N may be as follows. The reaction may begin with an electrophilic interaction of the Pd(II) with double bond followed by ether nucleophilic desilylation by Cl^- or deprotonation[7] by Et_3N in a competitive manner to afford **2** or **3a**, respectively.

We described here an efficient synthesis of (η^3-allyl)palladium complexes containing silyl group by the reaction of $PdCl_2(CH_3CN)_2$ with allylsilanes involving deprotonation instead of usual desilylation. Studies on the reaction of the [η^3-(silyl)allyl]palladium complexes thus obtained, in particular the complex **5** which might be an interesting precursor to trimethylenemethane palladium,[8] are in progress.

1-3 Experimental Section

General Procedures. ^1H NMR spectra were recorded on a JEOL-GSX-270 (270 MHz) spectrometer as solution in $CDCl_3$ with reference to $CHCl_3$ (δ 7.26). Melting points were determined on Mitamura Riken Kogyo micro melting point apparatus and are uncorrected. The characterization of **3a, 3b,** and **3e** was described in Chapter 3.

Reaction of Allyltrimethylsilane (1a) with $PdCl_2(CH_3CN)_2$. Under a nitrogen atmosphere, 255 mg (1 mmol) of $PdCl_2(CH_3CN)_2$ was suspended in 5 mL of dry CH_3CN. Allyltrimethyl-silane (**1a**, 114 mg, 1 mmol) was added and the mixture was stirred at 25 °C for 1 h. The reaction mixture was concentrated and the product was isolated with use of a column chromatography (Florisil, 15 mm i.d. x 200 mm length, CH_2Cl_2), and the eluent of yellow band was concentrated to give (η^3-allyl)palladium chloride (**2**) (165 mg, 90%).

Reaction of Allyltrimethylsilane with $PdCl_2(CH_3CN)_2$ in the Presence of Triethylamine. Preparation of [η^3-(1-trimethylsilyl)allyl]-palladium Chloride (3a). Under an atmosphere of nitrogen, 255 mg (1 mmol) of $PdCl_2(CH_3CN)_2$ and 303 mg (3 mmol) of triethylamine were dissolved in 5 mL of dry CH_3CN. Allyltrimethylsilane **1a** (342 mg, 3 mmol) was added and the mixture was stirred at 25 °C for 12 h. The reaction mixture was concentrated and separated with use of a

column chromatography (Florisil, 15 mm i.d. x 200 mm length, CH_2Cl_2/hexane = 1/1), and the eluent of yellow band was concentrated to give [η^3-(1-trimethylsilyl)allyl]palladium chloride (**3a**) (209 mg, 82%).

[η^3-(1-*t*-Butyldimethylsilyl)allyl]palladium Chloride (3c). The complex **3c** was prepared in benzene from **1c** by the method described above: Yield 21% (*syn/anti* = 75/25); mp 139-143 °C dec; ^{1}H NMR ($CDCl_3$) δ (*syn*) 0.14 (s, 3 H), 0.32 (s, 3 H), 0.91 (s, 9 H), 2.96 (d, J = 11.2 Hz, 1 H), 2.99 (d, J = 13.7 Hz, 1 H), 4.07 (d, J = 6.1 Hz, 1 H), 5.31 (ddd, J = 13.7, 11.2, 6.1 Hz, 1 H),; δ (*anti*) 0.25 (s, 3 H), 0.32 (s, 3 H), 0.86 (s, 9 H), 3.04 (d, J = 12.5 Hz, 1 H), 3.97 (d, J = 9.8 Hz, 1 H), 3.98 (d, J = 7.1 Hz, 1 H), 5.85 (ddd, J = 12.5, 9.8, 7.1 Hz, 1 H). Anal. Calcd for $C_9H_{19}ClPdSi$. C, 36.37; H, 6.44. Found, C, 36.23; H, 6.56.

[η^3-(2-Trimethylsilylmethyl)allyl]palladium Chloride (5). A mixture of **5**, **3e**, and **6** was obtained from **1b** by the method described above. The complex **5** was isolated with use of a column chromatography (silica gel 100-200 mesh, CH_2Cl_2/hexane = 1/1, R_f = 0.35) followed by recrystallization from CH_2Cl_2/hexane (1/1): Yield 16%; mp 148-152 °C dec; ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 9 H), 1.90 (s, 2 H), 2.74 (s, 2 H), 3.67 (s, 2 H). Anal. Calcd for $C_7H_{15}ClPdSi$. C, 31.24; H, 5.62. Found C, 30.92; H, 5.83.

1-4 References and Notes

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(6) Ketley, A. D.; Braatz, J. *J. Chem. Soc., Chem. Commun.* **1968**, 169: A suspension of 570 mg (5 mmol) of **1a**, 177 mg (1 mmol) of $PdCl_2$ and 887 mg (8.37 mmol) of $NaHCO_3$ in 2.5 mL of $CHCl_3$ was stirred for 5 h at room temperature. A mixture of **3a** (10%) and **2** (12%) was obtained.

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Chapter 2

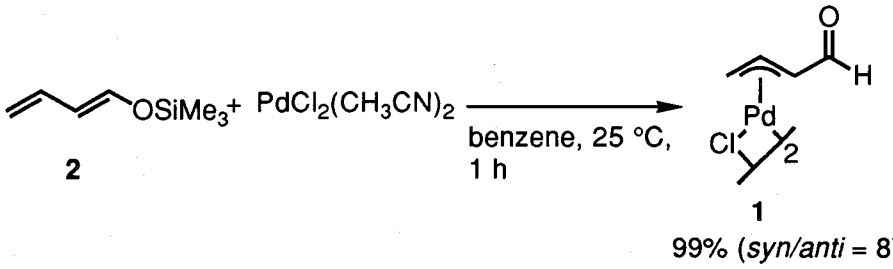
Convenient Synthesis of [η^3-1-(Formyl)allyl]- and [η^3-1-(Dimethoxymethyl)allyl]-palladium Chlorides

2-1 Introduction

The aldol reaction is one of the most powerful methods for carbon-carbon bond formation in organic synthesis. Aldehydes and acetals have been commonly used as the electrophilic acceptor in the aldol reaction. The range of aldehydes and acetals capable of undergoing aldol reactions as well as the stereochemical course of the reaction have been well investigated, especially in the case of the reactants having α-substituents. However, there are few reports dealing with the reaction of substrates whose α-substitutents are metal moieties.[1] It was anticipated that such aldol reactions might show new possibilities based on the bound metal. Thus, we initiated a study to develop a method for the preparation of such metal complexes. I describe here efficient access to η^3-allylpalladium complexes in which an aldehyde or an acetal function is attached at the allylic terminal carbon.

2-2 Results and Discussion

The simplest formyl compound of this sort may be η^3-1-(formyl)allylpalladium chloride **1**. This complex **1** has been reported in the study of the reaction of $PdCl_2$ with 1-methoxybutadiene, but no experimental details were given except for its ^1H NMR data.[2] Having studied the reaction of Pd(II) with a dienol silyl ether,[3] we examined the reaction of $PdCl_2(CH_3CN)_2$ with 1-siloxybutadiene **2** to obtain the desired complex **1**. Thus, treatment of dienol silyl ether **2** with $PdCl_2(CH_3CN)_2$ in dry benzene at room temperature for 1 h afforded η^3-1-(formyl)allylplladium chloride **1**[4] in a quantitative yield (99%, *syn/anti* = 87/13) (eq 1).

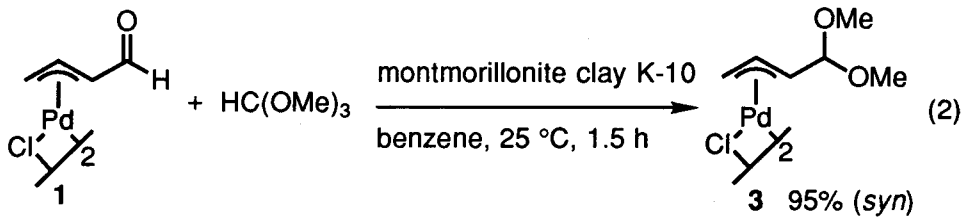


2 **1** (1)

99% (*syn/anti* = 87/13)

When treated with trimethyl orthoformate and montmorillonite clay K-10 in dry CH_2Cl_2[5] at room temperature for 1.5 h, **1** was converted to the desired complex, η^3-1-(dimethoxymethyl)allylpalladium chloride **3** (95%, only *syn* isomer) (eq 2). The exclusive formation of

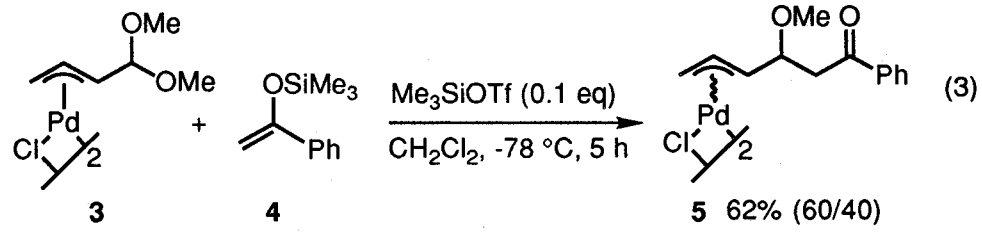
syn isomer will bring about some advantages from view point of organic synthesis.

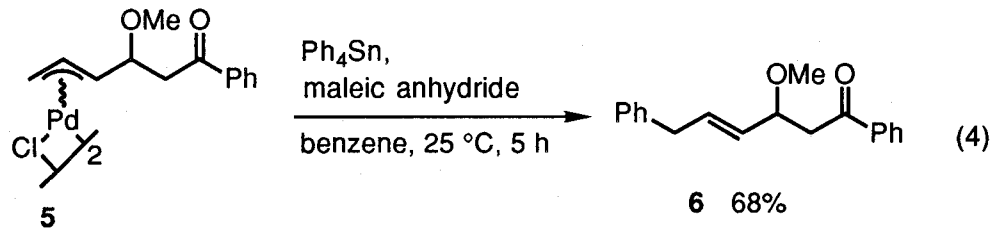


(2)

We then have just briefly examined the possibility of the use of an aldehyde complex **1** and an acetal complex **3** in aldol type reaction. In these complexes or their activated forms, four sites are available in principal for nucleophilic attack, these being two terminal carbon atoms of the allyl part,[6] carbonyl or acetal carbon atom, and metal center. Of the four sites, the acetal carbon atom of **3** was selectively attacked by an enol silyl ether as described below, while the complex **1** reacted only sluggishly under several types of standard reaction conditions. The acetal complex **3** reacted with an enol silyl ether **4** in the presence of Me_3SiOTf in CH_2Cl_2 at -78 °C for 5 h, to give an aldol product **5** (62%, major/minor = 60/40; eq 3). The two isomers of **5** correspond to diastereomers with respect to β- and γ-positions of the carbonyl and the both isomers exist in *syn* forms. Phenylation of **5** with Ph_4Sn in the presence of maleic anhydride[7] in dry benzene at 25 °C for 5 h gave *E*-olefin **6** (68%) exclusively (eq 4). An interesting

possibility of intervention of a cationic palladium (1-methoxybutadiene) complex[8] obtainable from **3** and Me_3SiOTf is not clear at this time. In conclusion, it is expected that the development of convenient methods for the preparation of (η^3-allyl)palladium (II) having a formyl or an acetal group will provide unique opportunities in aldol and organometallic chemistry.





2-3 Experimental Section

General Procedures. ^1H NMR spectra was recorded on a JEOL-GSX-270 (270 MHz) spectrometer as solution in $CDCl_3$ with reference to $CHCl_3$ (δ 7.26). Melting points were determined on Mitamura Riken Kogyo micro melting point apparatus and are uncorrected.

Synthesis of [η^3-1-(formyl)allyl]palladium Chloride (1). Under an atmosphere of nitrogen, dienol silyl ether **2** (1.53 g, 10 mmol) was added to the suspension of $PdCl_2(CH_3CN)_2$ (1.82 g, 7.1 mmol) in dry benzene (80 mL) at room temperature and the suspension was stirred for 1 h. The reaction mixture was concentrated in vacuo (5 mmHg) to give η^3-1-(formyl)allylplladium chloride **1** in a quantitative yield (1.47 g, 99%, *syn*/*anti* = 87/13): mp 142-143 °C dec; IR (KBr) 1699, 1695 cm^{-1}; ^1H NMR ($CDCl_3$) **1-*syn*** δ 3.44 (d, J = 12.6 Hz, 1 H), 3.86 (dd, J = 5.1, 10.9 Hz, 1 H), 4.35 (d, J = 7.3 Hz, 1 H), 5.97 (ddd, J = 12.6, 10.9, 7.3 Hz, 1 H), 9.65 (d, J = 5.1 Hz, 1 H), **1-*anti*** δ 3.97 (d, J = 13.7 Hz, 1 H), 4.39 (d, J = 7.5 Hz, 1 H), 5.02 (dd, J = 4.6, 5.7 Hz, 1 H), 5.68 (ddd, J = 13.7, 7.5, 5.7 Hz, 1 H), 9.02 (d, J = 4.6 Hz, 1 H). Anal. Calcd for C_4H_5OClPd: C, 22.77; H, 2.39; Cl, 16.81. Found: C, 23.09; H, 2.46; Cl, 16.64.

Transformation of 1 into [η^3-1-(dimethoxymethyl)-allyl]palladium Chloride (3). The complex **1** (1.06 g, 5 mmol), trimethyl orthoformate (7.5 g) and montmorillonite clay K-10 (5 g) were stirred in dry CH_2Cl_2 (25 mL) at room temperature for 1.5 h. The reaction mixture was filtered and concentrated to give yellow oil. The yellow oil was recrystallized with CH_2Cl_2/hexane to give [η^3-1-(dimethoxymethyl)allyl]-palladium chloride **3** (1.24 g, 95%, only *syn* isomer): mp 105-108 °C; ^1H NMR ($CDCl_3$) δ 3.03 (d, J = 12.2 Hz, 1 H),

3.34 (s, 3 H), 3.43 (s, 3 H), 3.58 (dd, J = 10.8, 2.2 Hz, 1 H), 4.04 (d, J = 6.8 Hz, 1 H), 4.63 (d, J = 2.2 Hz, 1 H), 5.65 (ddd, J = 12.2, 10.8, 6.8 Hz, 1 H). Anal. Calcd for $C_6H_{11}O_2ClPd$: C, 28.04; H, 4.31; Cl, 13.79. Found: C, 28.11; H, 4.33; Cl, 13.87.

Aldol reaction of 3 with enol silyl ether. A solution of the acetal complex **3** and an enol silyl ether **4** (384 mg, 2 mmol) in dry CH_2Cl_2 (5 mL) was cooled to -78 °C and Me_3SiOTf (44.4 mg, 0.2 mmol) was added. The reaction mixture was stirred at -78 °C for 5 h and warmed up to 25 °C. Then, the mixture was washed with saturated aqueous $NaHCO_3$ solution (15 mL) and dried over $MgSO_4$ for 3 h. The residue was separated with use of a column chromatography (silica gel 100-200 mesh, hexane/EtOAc = 2/1, R_f = 0.11) to give an aldol product **5** (426 mg, 62%, major/minor = 60/40): mp 61-63 °C dec; IR (KBr) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) **5-major** δ 3.01 (d, J = 12.4 Hz, 1 H), 3.34 (d, J = 5.4 Hz, 1 H), 3.39 (d, J = 7.8 Hz, 1 H), 3.46 (s, 3 H), 3.86 (dd, J = 11.2, 4.2 Hz, 1 H),4.01 (ddd, J = 7.8, 5.4, 4.2 Hz, 1 H), 4.02 (d, J = 6.6 Hz, 1 H), 5.58 (ddd, J = 12.4, 11.2, 6.6 Hz, 1 H), 7.3-8.1 (m, 5 H). **5-minor** δ 2.96 (d, J = 13.1 Hz, 1 H), 3.28 (d, J = 4.6 Hz, 1 H), 3.53 (d, J = 6.8 Hz, 1 H), 3.44 (s, 3 H), 3.94 (dd, J = 11.2, 2.9 Hz, 1 H),4.01 (ddd, J = 6.8, 4.6, 2.9 Hz, 1 H), 4.02 (d, J = 6.6 Hz, 1 H), 5.58 (ddd, J = 13.1, 11.2, 6.6 Hz, 1 H), 7.3-8.1 (m, 5 H). Anal. Calcd

for $C_{13}H_{15}OClPd$: C,45.24; H, 4.38. Found: C, 44.94; H, 4.36.

Phenylation of 6. To a solution of aldol product **5** (160 mg, 0.47 mmol) and maleic anhydride (91 mg, 0.93 mmol) in dry benzene (10 mL) was added Ph_4Sn (195 mg, 0.47 mmol) at 25 °C and the reaction mixture was stirred for 5 h and concentrated. The residue was separated with use of a column chromatography (silicagel 100-200 mesh, hexane/EtOAc = 6/1, R_f = 0.18) to give **6** (yield 68 %).; ^1H NMR ($CDCl_3$) δ 2.96 (d, J = 5.1 Hz, 1 H), 3.02 (d, J = 5.4 Hz, 1 H), 3.27 (s, 3 H), 3.33 (d, J = 7.3 Hz, 1 H), 3.39 (d, J = 7.8 Hz, 1 H), 4.26 (dddd, J = 7.8, 5.4, 5.1, 0.7 Hz, 1 H), 5.47 (ddt, J = 15.1, 7.8, 1.5 Hz, 1 H), 5.90 (dtd, J = 15.1, 6.8, 0.7 Hz, 1 H), 7.1-7.4 (m, 5 H), 7.5-8.0 (m, 5 H)

2-4 References and Notes

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(2) Andri, M. K.; Krylov, A. V.; Averochkin, N. E.; Belov, A. P. *Koord. Khim.* **1984**, *10*, 540.

(3) The reaction of $PdCl_2$ with 1-silyl-1-(siloxy)butadiene was found to give η^3-1-(silylcarbonyl)allylpalladium chloride (see chapter 3).

(4) Molybdenum and Ruthenium complexes analogous to **1** were also prepared by using the similar method. Benyunes, S. A.; Green, M.; Grimshire, M. J. *Organometallics* **1989**, *8*, 2268. Benyunes, S. A.; Day, J. P.; Green, M.; Al-Saadoon, A. W.; Waring, T. L. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1416.

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(6) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. Tsuji, J.; Minami, I. *Acc. Chem. Res.* **1987**, *20*, 140

(7) Kurosawa, H.; Ogoshi, S.; Kawasaki, Y.; Murai, S.; Miyoshi, M.; Ikeda, I. *J. Am. Chem. Soc.* **1990**, *112*, 2813.

(8) (a) No aldol reaction occurred between **3** and **4** in the absence of Me_3SiOTf. (b) Treatment of analogous acetal-substituted (η^3-allyl)molybdenum complexes with HBF_4 led to isolation of cationic diene-molybdnum complexes, which in turn reacted with nucleophiles to give (η^3-allyl)metal analogous to **5**.[9]

(9) Hasson, S.; Miller, J. F.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 9660.

Chapter 3

Reaction of 1-Silyl-Dienol Silyl Ethers with Palladium(II) Complexes. Novel Formation of Several Types of (η^3-Allyl)palladium(II) Complexes via Versatile Complex [η^3-1-(Silylcarbonyl)allyl]palladium Chloride

3-1 Introduction

Extensive studies have been done on the reactions of (η^3-allyl)metal complexes.[1] In contrast, however, the chemistry of the (η^3-allyl)metal complexes in which a functional group is attached to the allyl moiety still remains to be studied. In view of this, the studies on the carbonyl groups attached at terminal carbons of an η^3-allyl system are very interesting. However, there have been only a few examples of the utilization of such carbonyl groups, i.e. those in (η^3-allyl)molybdenum[2] and (η^3-allyl)ruthenium complexes[3]. No such utilization in (η^3-allyl)palladium has yet been reported.

I thought it very interesting to study reactions of Pd(II) salts with the 1-silyl dienol silyl ethers **1**, since these reactions may provide a new entry to (η^3-allyl)palladium complexes bearing carbonyl functionalities.[4] In addition, the dienol silyl ether **1** contains various functional groups such as diene, dienol, enol silyl ether, and vinylsilane as well as the latent functionality of ketone, acyl silane, and enone. These

multiple functionalites, when coupled with the oxidation/reduction properties of Pd(II) salts, would bring about an unique opportunity to find a variety of new reactions.

In this chapter, I wish to report detailed aspects of these reactions giving various (η^3-allyl)palladium complexes, which heavily depends on the type of Pd(II) salts, solvents, and the acidity of the medium and the possible mechanisms of all reactions.

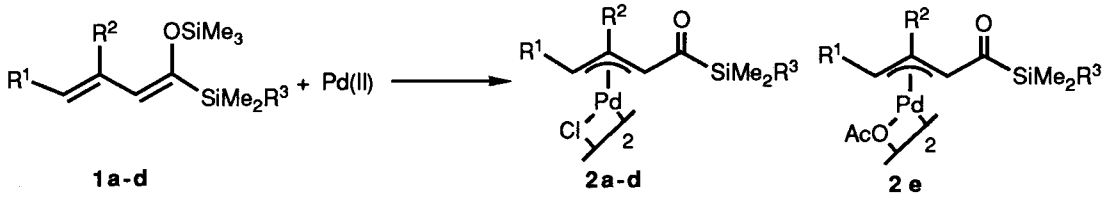
3-2 Results and Discussion

Simple Transmetallation.

In the reaction of 1-silyl dienol silyl ethers with Pd(II) salts, a simple transmetallation to give [η^3-1-(silylcarbonyl)allyl]palladium occurred under only limited conditions. Thus, the reaction of dienol silyl ethers **1a-d** with Li_2PdCl_4 in the presence of Li_2CO_3 in MeOH gave [η^3-1-(silylcarbonyl)allyl]palladium chlorides **2a-d** (85%, 33%, 72%, 30%) together with a small amount of [η^3-1-(methoxycarbonyl)allyl]palladium chlorides **3**[7] (4% from **2a**, 2% from **2b**) (Table I). The same reaction occurred in THF to give **2a** (42%) together with small amounts of [η^3-1-(silyl)allyl]palladium chloride **4a** (2%), which is a formal decarbonylation product of **2a**. Complex **2a** was also obtained from $PdCl_2(PhCN)_2$ and the mercury compound $Me_3SiC(O)CH=CHCH_2HgOAc$, prepared from **1a** and $Hg(OAc)_2$, in benzene. The reaction of **1a** with $Pd(OAc)_2$ in benzene also involved simple transmetallation to give

2e. The use of Li_2PdCl_4 or $Pd(OAc)_2$ is essential to the simple transmetallation, for the analogous reactions employing $PdCl_2(PhCN)_2$ resulted in different products (see below).

Table I. Simple Transmetallation of Dienol Silyl Ethers with Pd(II) salts



1a-d **2a-d** **2e**

dienol silyl ether		Pd(II) salt	additive	solvent	product	yield,[a] %
1a	$R^1=R^2=H$ $R^3=Me$	Li_2PdCl_4	Li_2CO_3	MeOH	**2a**	85[b] (*syn*)
1b	$R^1=R^2=H$ $R^3=Ph$	Li_2PdCl_4	Li_2CO_3	MeOH	**2b**	33[c] (*syn*)
1c	$R^1=H$ $R^2=R^3=Me$	Li_2PdCl_4	Li_2CO_3	MeOH	**2c**	72 (*syn/anti* = 27/73)
1d	$R^1=Ph$ $R^2=H$ $R^3=Me$	Li_2PdCl_4	Li_2CO_3	MeOH	**2d**	30 (*syn*)
1a		Li_2PdCl_4	Li_2CO_3	THF	**2a**	42[d] (*syn*)
1a		Li_2PdCl_4		THF	**2a**	41[e] (*syn*)
1a		$Pd(OAc)_2$		C_6H_6	**2e**	51 (*syn*)

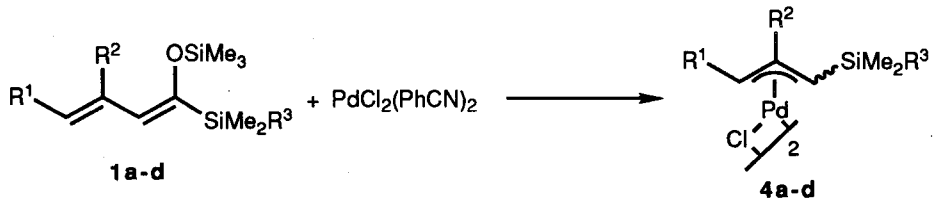
[a] All yields refer to isolated yields. [b] A small amount of **3** (4%) was obtained. [c] A small amount of **3** (2%) was obtained. [d] A small amount of **4a** (2%) was obtained. [e] A small amount of **4a** (7%) was obtained.

Decarbonylation.

In the reaction of **1a** in THF, changing the Pd(II) salt from Li_2PdCl_4 to $PdCl_2(PhCN)_2$ led to the exclusive formation of **4a** (44%). Moreover, similar treatment of **1a-d** with $PdCl_2(PhCN)_2$ in benzene also afforded [η^3-1-(silyl)allyl]palladium chlorides **4a-d** (76%, 57%, 41%,

77%; Table II). The nature of the solvent is important here, for the reaction of $PdCl_2(PhCN)_2$ with **1** in MeOH took a still different course (see below).

Table II. Decarbonylative Reactions of Dienol Silyl Ethers with $PdCl_2(PhCN)_2$



1a-d **4a-d**

dienol silyl ether	solvent	product	yield,[a] % (*syn/anti*)
1a	THF	**4a**	44 (80/20)
1a	C_6H_6	**4a**	76 (73/27)
1b	C_6H_6	**4b**	57 (85/15)
1c	C_6H_6	**4c**	41 (33/67)
1d	C_6H_6	**4d**	77 (74/26)

[a] All yields refer to isolated yields.

When treated with a catalytic amount of $PdCl_2(PhCN)_2$ in benzene, **2a-c** underwent decarbonylation to give **4a-c** (85%, 43%, 43%; Table III). It then may well be that, in the decarbonylation reaction of dienol silyl ether **1** with $PdCl_2(PhCN)_2$ in benzene (Table II), the formation of **2** is slow so that the decarbonylation catalyst $PdCl_2(PhCN)_2$ is always present to force most of the **2** formed to undergo decarbonylation.

Table III. Decarbonylation of 2a-c Catalyzed by $PdCl_2(PhCN)_2$[a]

compound	time, h	product	yield,[b] % (*syn/anti*)
2a	12	**4a**	86 (71/29)
2b	24	**4b**	43 (83/17)
2c	70	**4c**	43 (59/41)

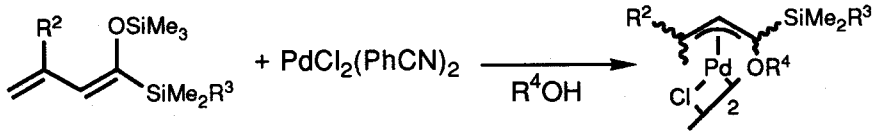
[a] Reaction conditions: **2** (0.1 mmol), $PdCl_2(PhCN)_2$ (0.01 mmol), C_6D_6 (1 mL), 25 °C. [b] NMR yields.

This reaction is the first example of decarbonylation from formal homoacyl metal complexes. However, when **6**[8] and **7**,[9] analogous to **2a**, were treated with a catalytic amount of $PdCl_2(PhCN)_2$, decarbonylation did not occur. Thus, the decarbonylation needs the trimethylsilyl group attached to the carbonyl carbon.

Two-Electron Reduction.

The reaction of excess amounts of dienol silyl ethers **1a-c** with $PdCl_2(PhCN)_2$ (**1**/Pd=2/1) in MeOH afforded the unexpected complexes [η^3-1-(methoxy)-3-(methyl)-1-(silyl)allyl]palladium chloride (**5a-c**; 96%, 41%, 25%), no **2a-c** and **4a-c** being obtained (Table IV). These complexes were composed of some *syn-anti* isomers on the basis of ^1H NMR spectroscopy (see Experimental Section). However, we could not determine the exact disposition of the substituents with respect to the *syn* and *anti* sites. Note that the complex **5** is derived by a formal two-electron reduction of **2**. Similar reactions occurred also in EtOH and in benzyl alcohol to give the corresponding complexes **5d** and **5e** (95%, 47%; Table IV). There are only a small number of such complexes known that contain a terminal η^3-allyl carbon-oxygen bond (M = Pd, Ni, Fe).[10]

Table IV. Reactions in Alcohol of Dienol Silyl Ethers with $PdCl_2(PhCN)_2$

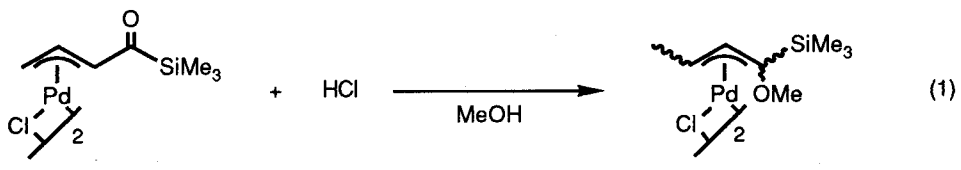


1a-c **5a-e**

dienol silyl ether	solvent (R^4OH)	product	yield,[a] %
1a	MeOH	**5a**	96
1b	MeOH	**5b**	41
1c	MeOH	**5c**	25
1a	EtOH	**5d**	94
1a	$PhCH_2OH$	**5e**	47

[a] All yields refer to isolated yields.

It is conceivable that the reaction of Table IV initially generated the complex **2** and Me_3SiCl, the latter of which might have reacted with MeOH to give HCl. Thus, we treated **2a** with 1 equiv of HCl (from Me_3SiCl) in MeOH resulting in formation of the complex **5a** (33%; eq 1). However, the complexes **6** and **7**, analogous to **2a-c**, did not undergo the same reaction. Thus, the two-electron reduction of the η^3-allyl moiety also occurred only in **2**, in which silyl groups are attached at the carbonyl carbon.

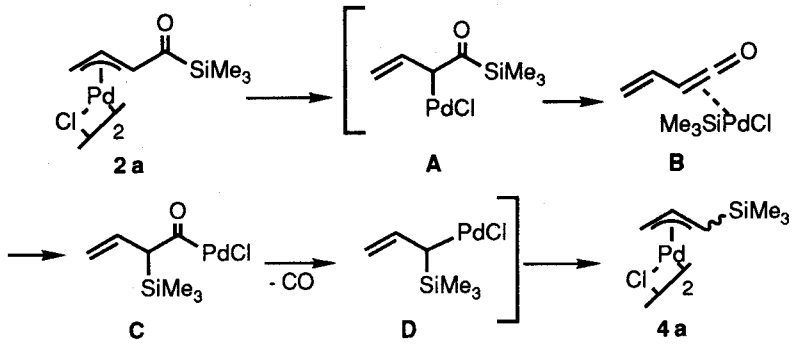


2a **5a** 33% (1)

Mechanistic Study.

The decarbonylation reaction may be explained by a few mechanisms. The most plausible mechanism involves a palladium-silicon interaction. Scheme I outlines a possible mechanism of the decarbonylation reaction.

Scheme I. Plausible Mechanism of Decarbonylation

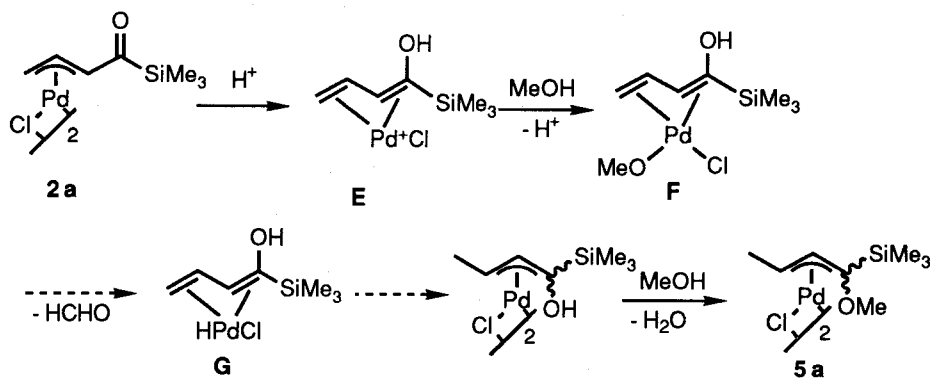


The silylcarbonyl-substituted complex **2a** is converted to the η^1-allyl complex **A**, in which β-elimination of the trimethylsilyl group[11] affords the vinyl ketene complex intermediate **B**. No intermolecular exchange of the coordinated ketene would be occurring, because treatment of a mixture of **2b** and **2c** with a catalytic amount of $PdCl_2(PhCN)_2$ afforded only **4b** and **4c**, but no crossover products. Subsequent addition of the silyl-palladium moiety to the ketene in the reverse direction affords acyl palladium complex **C**, from which decarbonylation gives rise to the (η^1-allyl)palladium species **D**[12] and then (η^3-allyl)palladium complex **4a**. As an alternative, fragmentation of the vinylketene ligand in **B** into vinylcarbene and CO ligands, followed by

insertion of the carbene into Si-Pd leading to **D**, can be envisaged.[13] A possible role of $PdCl_2$ species in catalyzing decarbonylation is to convert **2a** to the η^1-allyl intermediate.

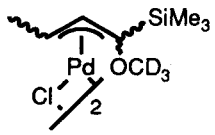
Formation of **5** from **2** may be explained also by a few mechanisms. Any satisfactory mechanism must involve a source of electrons in order to be compatible with the apparently imbalanced stoichiometry of eq 1. Scheme II assumes MeOH as a reductant. In this scheme, the initial protonation converts **2a** to the dienol palladium complex **E**.[14]

Scheme II. Unlikely Mechanism



A similar conversion has been observed in the (η^3-allyl)molybdenum complex.[2a] An attack of the methoxy group on the palladium cation center gives the methoxy palladium species **F**. Subsequent β-elimination from the methoxy group[15] gives the key intermediate **G**, which can be converted to **5a**. According to this mechanism, **2a** would afford **5a** even with a catalytic amount of HCl. We assert below that this is not the case.

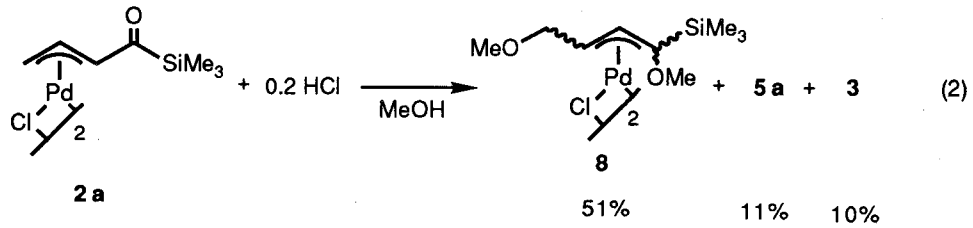
First, the reaction of **2a** (0.1 mmol) and benzyl alcohol (0.3 mmol) with 1 equiv of HCl in $CDCl_3$ gave **5e** and no benzaldehyde.



9

Moreover, treatment of **1a** with $PdCl_2(PhCN)_2$ in CD_3OH resulted in **9**, where only the CH_3O- group was changed to the CD_3O- group and no deuterium incorporation in the rest of the allyl ligand was detected. From these results, it is clear that MeOH is not a source of electrons.

Second, when treated with a catalytic amount of HCl in MeOH, **2a** unexpectedly afforded the [η^3-1-(methoxy)-3-(methoxymethyl)-1-(silyl)allyl]palladium chloride complex **8** (51%), together with a smaller amount of **5a** (11%) and the [η^3-1-(methoxycarbonyl)allyl]palladium chloride complex **3** (10%; eq 2).



2a **8** 51% 11% 10%

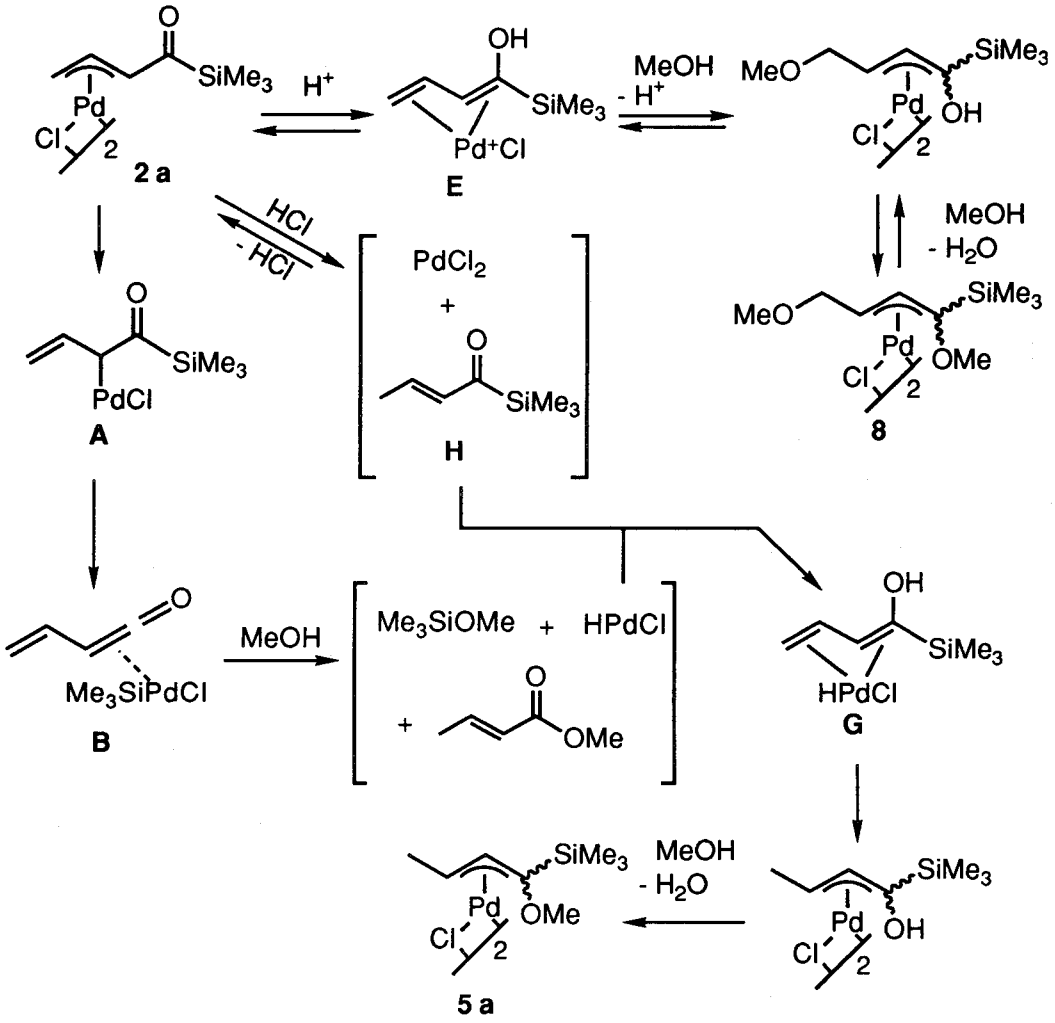
The complex **8** was transformed into **5a** (27%) with a stoichiometric amount of HCl in MeOH. The complex **8** was also transformed into **5d** with a stoichiometric amount of HCl in EtOH (11%). These facts suggest that in the presence of HCl the formation of **8** from **2a** was reversible. The formation of **8** may be explained by the attack of methanol directly at the diene of **E**,[16] rather

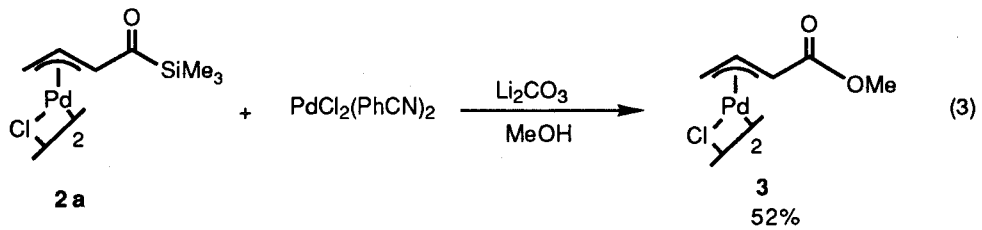
than the Pd atom of **E**. In any case, it is clear that 1 equiv of HCl is necessary for the formation of **5a**.

Scheme III shows a more plausible mechanism. In the presence of HCl, **2a** could generate $PdCl_2$ and the α,β-unsaturated acylsilane **H**. As suggested above, this Pd(II) species would catalytically convert **2a** to the ketene-palladium complex intermediate **B**. The intermediate **B** might react with MeOH to give the key species HPdCl. Coordination of the dienol of **E** or **H** to HPdCl gives **G**, which is eventually transformed into **5a** by hydride attack and subsequent alcohol exchange. In this mechanism, HCl is not regenerated and the η^3-(silylcarbonyl)allyl ligand is a source of electrons. However, we failed to detect any product expected to be derived from vinylketene or any other intermediate in the reactions of both table IV and eq 1.

When the reaction of **2a** with 1 equivalent of $PdCl_2(PhCN)_2$ in MeOH was carried out in the presence of Li_2CO_3, a considerable amount of **3** was obtained (52%; eq 3). The formation of **3** could arise via the generation of methyl crotonate through trapping of vinylketene intermediate **B** by MeOH.

Scheme III. Plausible Mechanism





3-3 Experimental Section

General Procedures. ^1H 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 reference to $CHCl_3$ (δ 7.26). IR spectra were recorded on a Hitachi 270-50 infrared spectrophotometer as KBr pellets. Melting points were determined on a Mitamura Riken Kogyo micro melting point apparatus and are uncorrected.

Synthesis of 1-Trimethylsilyl-1-trimethylsiloxy-butadiene (1a). An *n*-hexane solution of *n*-BuLi (1.6 M, 48 mmol) was added to a solution of 3.8 g (33.3 mmol) of allyltrimethylsilane in 13.3 mL of dry TMEDA and 56 mL of dry THF at 0 °C under an atmosphere of argon. The solution was stirred for 6 h. After three evacuations of argon gas under vacuum followed by substitution with carbon monoxide, the reaction mixture was warmed to 25 °C and stirred under an atmosphere of carbon monoxide for 12 h. Then 7.0 mL (6.0 g, 55 mmol) of Me_3SiCl was added to the mixture at 0 °C and the mixture was stirred for 1 h. The mixture was poured into 200 mL of saturated aqueous sodium bicarbonate solution. The aqueous layer was extracted with three 100 mL portions of Et_2O, and the ether solution dried over anhydrous magnesium sulfate. The solvents were removed under reduced pressure to provide the mixture of TMEDA and dienol silyl ether **1a**. TMEDA was distilled off from dienol silyl ether **1a** at 760

mmHg very carefully. Then the dienol silyl ether **1a** was obtained by distillation (50 mmHg, 100 °C) in 70% isolated yield: IR (neat) 1630, 1570 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (s, $SiMe_3$), 0.23 (s, $SiMe_3$).

4-Phenyl-1-trimethylsilyl-1-trimethylsiloxybutadiene (1d). Under an argon atmosphere, to a solution of 1.06 g (4.5 mmol) of cinnamyltrimethylsilane and 2 mL of TMEDA in 8.5 mL of dry THF was added 4.2 mL (6.72 mmol, 1.6 M/hexane) of *n*-BuLi at -78 °C and this mixture was stirred for 30 min. The reaction mixture was warmed to 25 °C and stirred under 30 atm of CO for 12 h. Under a nitrogen atmosphere, 1.2 mL (9.5 mmol) of Me_3SiCl was added to the reaction mixture at 0 °C. The mixture was washed with 60 mL of saturated $NaHCO_3$ (aq) and extracted with three 30 mL portions of Et_2O. The Organic layer was dried over $MgSO_4$ and concentrated. The residue was separated with use of a column (silica gel 100-200 mesh, 40 mm i.d. x 200 mm length, CH_2Cl_2 /hexane = 1/10, R_f = 0.18) to afford **1d** in 39% isolated yield: IR (neat) 2984, 1600, 1570 cm^{-1}, ^1H NMR ($CDCl_3$) δ 0.16 (s, 9 H), 0.27 (s, 9 H), 5.93 (d, J = 10.7 Hz, 1 H), 6.48 (d, J = 15.9 Hz, 2 H), 7.12 (dd, J = 10.7, 15.9 Hz, 1 H), 7.31 (m, 3 H), 7.38 (m, 2 H).

Reaction of 1-Trimethylsilyl-1-trimethylsiloxybutadiene 1a with Li_2PdCl_4. Preparation of [η^3-1-(Trimethylsilylcarbonyl)allyl]palladium Chloride (2a-*syn*). A suspension of 885 mg (5 mmol) of $PdCl_2$, 440

mg (10 mmol) of anhydrous LiCl, and 370 mg (5 mmol) of Li_2CO_3 in 25 mL of anhydrous MeOH was stirred for 2 h an under atmosphere of argon at 25 °C. Then, 1500 mg (7 mmol) of dienol silyl ether **1a** was added to the suspension and the mixture was stirred for 12 h. The reaction mixture was filtered under an atmosphere of argon. The filtrate was concentrated in vacuo (5 mmHg), and the concentrate was separated with use of a column (Florisil, 15 mm i.d. x 300 mm length, CH_2Cl_2). Orange fractions were concentrated under reduced pressure (5 mmHg) to afford an orange oil. Into this oil was poured 50 mL of hexane, and the mixture cooled to -10 °C. After 20 h, the orange solids obtained were washed with three 10 mL portions of hexane. The complex **2a** was obtained with a small amount of **3** in 85% (1203 mg, **2a**/**3** = 95/5) isolated yield: mp 113-115 °C dec; IR (KBr) 1608 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.25 (s, 9 H), 3.22 (d, J = 12.7 Hz, 1 H), 4.08 (d, J = 10.7 Hz, 1 H), 4.21 (d, J = 6.8 Hz, 1 H), 5.95 (ddd, J = 12.7, 10.7, 6.8 Hz, 1 H). Anal. Calcd for $C_7H_{13}OClPdSi$: C, 29.70; H, 4.63; Cl, 12.52. Found: C, 29.42; H, 4.42; Cl, 12.39.

[η^3-1-(Dimethylphenylsilylcarbonyl)allyl]palladium Chloride (2b-*syn*) was prepared with use of the procedure for **2a**: Yield 33%; mp 124-125 °C dec; IR (KBr) 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.52 (s, 3 H), 0.59 (s, 3 H), 3.22 (d, J = 12.7 Hz, 1 H), 3.95 (d, J = 11.0 Hz, 1 H), 4.12 (d, J = 7.1 Hz, 1 H), 5.84 (ddd, J = 12.7, 11.0, 7.1

Hz, 1 H) 7.41 (m, 3H) 7.61 (m, 2H). Anal. Calcd for $C_{12}H_{15}OClPdSi$: C, 41.75; H, 4.38. Found C, 41.55; H, 4.44.

[η^3-2-(Methyl)-1-(trimethylsilylcarbonyl)allyl]-palladium Chloride (2c-*syn*,*anti*) was prepared with use of the procedure for **2a**: Yield 72% (*syn/anti* = 27/73); mp 97-99 °C dec; IR (KBr) 1602 cm^{-1}; ^1H NMR ($CDCl_3$) **2c-*syn*** δ 0.23 (s, 9 H), 2.45 (s, 3 H), 2.98 (s, 1 H), 3.86 (s, 1 H), 3.94 (s, 1 H), **2c-*anti*** δ 0.27 (s, 9 H), 2.13 (s, 3 H), 3.90 (s, 1 H), 4.05 (s, 1 H), 5.19 (s, 1 H). Anal. Calcd for $C_8H_{15}OClPdSi$: C, 32.34; H, 5.09; Cl, 11.93. Found: C, 31.79; H, 5.13; Cl, 11.72.

[η^3-3-(Phenyl)-1-(trimethylsilylcarbonyl)allyl]-palladium Chloride (2d-*syn*) was prepared with use of the procedure for **2a**: Yield 30% (*mixture*); mp 142-144 °C dec; IR (KBr) 1613 cm^{-1}; ^1H NMR ($CDCl_3$) **2d-*syn*** δ 0.18 (Br, 9 H), 4.13 (Br, 1 H), 4.94 (Br, 1 H), 6.28 (Br, 1 H). Anal. Calcd for $C_{13}H_{17}OClPdSi$: C, 43.47; H, 4.77. Found: C, 43.45; H, 4.72.

Reaction of 1-(Trimethylsilyl)-1-(trimethylsiloxy)butadiene (1a) with $Hg(OAc)_2$: Dienol silyl ether **1a** (214 mg, 1 mmol) was added to a solution of 320 mg (1 mmol) of $Hg(OAc)_2$ in 5 mL of anhydrous MeOH, and the reaction mixture was stirred for 30 min. The reaction mixture was concentrated in vacuo (5 mmHg), and the

concentrate was extracted with three 3 mL portions of benzene. 10 mL of *n*-hexane was poured into the benzene solution, and the solution was cooled to -10 °C. After 12 h, yellow solids were obtained and washed with three 10 mL portions of *n*-hexane. The compound $Me_3SiC(O)CH=CHCH_2HgOAc$ was obtained in 78% (311 mg) isolated yield: IR (Nujol) 1635 cm^{-1} ; ^1H NMR ($CDCl_3$) δ 0.26 (s, 9 H), 2.04 (s, 3 H), 2.87 (d, J = 9.0 Hz, 2 H), 6.37 (d, J = 15.6 Hz, 1 H), 6.88 (dt, J = 15.6, 9.0 Hz, 1 H).

Reaction of $Me_3SiC(O)CH=CHCH_2HgOAc$ with $PdCl_2(PhCN)_2$. To a C_6D_6 solution (0.5 mL) of 40 mg (0.10 mmol) of $Me_3SiC(O)CH=CHCH_2HgOAc$ was added 30 mg (0.08 mmol) of $PdCl_2(PhCN)_2$. After 48 h, the reaction mixture was measured by ^1H NMR spectra to show almost quantitative formation of **2a**.

Reaction of 1-(Trimethylsilyl)-1-(trimethylsiloxy)butadiene (1a) with $Pd(OAc)_2$. Preparation of [η^3-1-(Trimethylsilylcarbonyl)allyl]palladium Acetate (2e-*syn*). The Pd(II) salt in preparation of **4a** was changed from $PdCl_2(PhCN)_2$ to $Pd(OAc)_2$ to give [η^3-1-(Trimethylsilylcarbonyl)allyl]palladium acetate in 51% isolated yield: mp 130 °C dec; IR (KBr) 1610, 1571 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.19 (s, 9 H), 1.94 (s, 3H) 3.30 (d, J = 12.5 Hz, 1 H), 3.84 (d, J = 7.1 Hz, 1 H), 4.21 (d, J = 11.0 Hz, 1 H), 6.39 (ddd, J = 12.5, 7.1, 11.0 Hz, 1 H).

Anal. Calcd for $C_9H_{16}O_3SiPd$: C, 35.24; H, 5.26. Found: C, 35.02; H, 5.22.

Reaction of 1-(Trimethylsilyl)-1-(trimethylsiloxy)butadiene 1a with $PdCl_2(PhCN)_2$. Preparation of [η^3-(1-Trimethylsilyl)allyl]palladium Chloride (4a-*syn,anti*). Under an atmosphere of argon, 214 mg (1 mmol) of dienol silyl ether **1a** was added to a suspension of 384 mg (1 mmol) of $PdCl_2(PhCN)_2$ in 10 mL of anhydrous benzene and the mixture stirred for 6 h at 25 °C. The reaction mixture was filtered and the yellow solution was concentrated in vacuo (5 mmHg) to give yellow solids. These were washed with three 10 mL portions of hexane. The complex **4a** was obtained in 76% (183 mg, *syn/anti* = 73/27) isolated yield: mp 165-170 °C dec; IR (KBr) no absorption at 1600-1800 cm^{-1}; ^1H NMR ($CDCl_3$) **4a-*syn*** δ 0.20 (s, 9 H), 2.96 (d, J = 11.3 Hz, 1 H), 3.05 (d, J = 13.4 Hz, 1 H), 4.07 (d, J = 6.1 Hz, 1 H), 5.30 (ddd, J = 11.3, 13.4, 6.1 Hz, 1 H), **4a-*anti*** δ 0.23 (s, 9 H), 3.09 (d, J = 12.2 Hz, 1 H), 3.97 (d, J = 7.2 Hz, 1 H), 4.07 (d, J = 9.8 Hz, 1 H), 5.75 (ddd, J = 12.2, 7.2, 9.8 Hz, 1 H). Anal. Calcd for $C_6H_{13}ClPdSi$: C, 28.25; H, 5.14. Found: C, 28.66; H, 5.06.

[η^3-1-(Dimethylphenylsilyl)allyl]palladium Chloride (4b-*syn,anti*) was prepared with use of the procedure for **4a**: Yield 57% (*syn/anti* = 85/15); mp 87-88 °C; IR (KBr) no absorption at 1600-1800 cm^{-1}; ^1H NMR ($CDCl_3$) **4b-*syn*** δ 0.50 (s, 3 H), 0.52 (s, 3 H), 3.02 (d, J = 11.5 Hz,

1 H), 3.17 (d, J = 13.7 Hz, 1 H), 4.09 (d, J = 6.4 Hz, 1 H), 5.32 (ddd, J = 11.5, 13.7, 6.4 Hz, 1 H) 7.37 (m, 3H) 7.60 (m, 2H), **4b-*anti*** δ 0.55 (s, 3 H), 0.59 (s, 3 H), 2.91 (d, J = 12.5 Hz, 1 H), 3.91 (d, J = 7.3 Hz, 1 H), 4.12 (d, J = 9.3 Hz, 1 H), 5.82 (ddd, J = 12.5, 7.3, 9.3 Hz, 1 H) 7.37 (m, 3 H) 7.60 (m, 2 H). Anal. Calcd for $C_{11}H_{15}ClPdSi$: C, 41.65; H, 4.77; Cl, 11.12. Found: C, 41.52; H, 4.78; Cl, 11.10.

[η³-2-(Methyl-1-trimethylsilyl)allyl]palladium Chloride (4c-*syn,anti*) was prepared with use of the procedure for **4a**: Yield 41% (*syn/anti* = 33/67); mp 108-109 °C; IR (KBr) no absorption at 1600-1800 cm^{-1}; ^1H NMR ($CDCl_3$) **4c-*syn*** δ 0.24 (s, 9 H), 2.12 (s, 3 H), 2,75 (s, 1 H), 2.81 (s, 1 H), 3.76 (s, 1 H), **4c-*anti*** δ 0.21 (s, 9 H), 2.17 (s, 3 H), 2.92 (s, 1 H), 3.87 (s, 1 H), 3,87 (s, 1 H). Anal. Calcd for $C_7H_{15}ClPdSi$: C, 31.24; H, 5.62; Cl, 13.17. Found: C, 31.55; H, 5.63; Cl, 13.31.

[η³-3-(Phenyl)-1-(trimethylsilyl)allyl]palladium Chloride (4d-*syn*, *anti*) was prepared with use of the procedure for **4a**: Yield 77% (*syn/anti* = 74/26); mp 188-190 °C dec; IR (KBr) no absorption at 1600-1800 cm^{-1}; ^1H NMR ($CDCl_3$) **4d-*syn*** δ 0.19 (s, 9 H), 3.07 (d, J = 13.7 Hz, 1 H), 4.53 (d, J = 10.7 Hz, 1 H), 5.62 (dd, J = 13.7, 10.7 Hz, 1 H), 7.25 (m, 3 H), 7.47 (m, 2 H). **4d-*anti*** δ 0.28 (s, 9 H), 3.90 (d, J = 9.5 Hz, 1 H), 4.66 (d, J = 11.7 Hz, 1 H), 6.10 (dd, J = 9.5, 11.7 Hz, 1 H), 7.25 (m,

3 H), 7.47 (m, 3 H). Anal. Calcd for $C_{12}H_{17}ClPdSi$: C, 43.52; H, 5.17. Found: C, 43.55; H, 5.24.

Crossover Experiment. A mixture of 17.3 mg of **2b** (0.05 mmol), 29.7 mg of **2c** (0.1 mmol), and 5.7 mg of $PdCl_2(PhCN)_2$ (0.015 mmol) was dissolved in 1.0 mL of C_6D_6. After 24 h at 25 °C, the reaction mixture was examined by ^1H NMR (**2b** 9%, **4b** 77% (*syn/anti* = 83/17); **2c** 70%, **4c** 29% (*syn/anti* = 59/41)).

Reaction of 1-(Trimethylsilyl)-1-(trimethylsiloxy)butadiene 1a with $PdCl_2(PhCN)_2$. Preparation of [η^3-1-(Methoxy)-3-(methyl)-1-(trimethylsilyl)-allyl]palladium Chloride (5a). Under an atmosphere of argon, 428 mg (2 mmol) of dienol silyl ether **1a** was added to a suspension of 384 mg (1 mmol) of $PdCl_2(PhCN)_2$ in 5 mL of anhydrous MeOH and the mixture was stirred for 12 h at 25 °C. The reaction mixture was filtered and the red solution was concentrated in vacuo (5 mmHg). The concentrate was separated with use of column (Florisil, 15 mm i.d. x 200 mm length, CH_2Cl_2). The yellow fraction was concentrated in vacuo (0.5 mmHg) to give yellow solids **5a** in 96% (292 mg) isolated yield: mp 145-150 °C dec; IR (KBr) no absorption at 1600-1800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.31 (s, 9 H), 1.23 (d, J = 6.1 Hz, 3 H), 3.47 (dq, J = 6.1, 11.2 Hz, 1 H), 3.57 (s, 3 H), 5.30 (d, J = 11.2 Hz, 1 H). The peaks at δ 0.31 and 3.57 split into four peaks (δ 0.273, 0.300, 0.312, 0.324; 3.538, 3.562,

3.573, 3.560), respectively, at -30 °C. Anal. Calcd for $C_8H_{17}OClPdSi$: C, 32.12; H, 5.73; Cl, 11.85. Found: C, 32.31; H, 5.74; Cl, 11.70.

[η^3-1-(Methoxy)-3-(methyl)-1-(dimethylphenylsilyl)allyl]palladium Chloride (5b) was prepared with use of the procedure for **5a**: Yield 41%; mp 142 °C dec; IR (KBr) No absorption at 1600-1800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.56 (s, 3 H), 0.81 (s, 3 H), 1.12 (d, J = 5.6 Hz, 3 H), 3.13 (dq, J = 11.0, 5.6 Hz, 1 H), 3.61 (s, 3 H), 5.34 (d, J = 11.2 Hz, 1 H), 7.38 (m, 3 H), 7.74 (m, 2 H). The peak at δ 0.81 splits into four peaks (δ 0.723, 0.740, 0.825, 0.838) at -40 °C. Anal. Calcd for $C_{13}H_{19}OClPdSi$: C, 43.22; H, 5.30; Cl, 9.81. Found: C, 43.44; H, 5.29; Cl, 9.72.

[η^3-1-(Methoxy)-3,3-(dimethyl)-1-(trimethylsilyl)-allyl]palladium Chloride (5c) was prepared with use of the procedure for **5a**: Yield 25% (major/minor = 67/33); mp 119-123 °C dec; IR (KBr) no absorption at 1600-1800 cm^{-1}; ^1H NMR ($CDCl_3$) (Major) δ 0.45 (s, 9 H), 1.24 (s, 3 H), 1.39 (s, 3 H), 3.51 (s, 3 H), 5.00 (s, 1 H) (Minor) δ 0.31 (s, 9 H), 1.44 (s, 3 H), 1.58 (s, 3 H), 3.57 (s, 3 H), 4.24 (s, 1 H). Anal. Calcd for $C_9H_{19}OClPdSi$: C, 34.51; H, 6.11. Found: C, 34.60; H, 6.31.

[η^3-1-(Ethoxy)-3-(methyl)-1-(trimethylsilyl)-allyl]palladium Chloride (5d) was prepared with use of the procedure for **5a**: Yield 94%; mp 150-155 °C dec; IR (KBr) no absorption at 1600-1800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.33 (s, 9 H), 1.21 (d, J = 6.1 Hz, 3 H), 1.24 (t, J = 6.4 Hz, 3 H), 3.43 (dq, J = 11.2, 6.8 Hz, 1 H), 3.83 (m, J = 6.4 Hz, 2 H), 5.26 (d, J = 11.2 Hz, 1 H). The peak at δ 0.33 splits into four peaks (δ 0.260, 0.282, 0.290, 0.317) at -40 °C. Anal. Calcd for $C_9H_{19}OClPdSi$: C, 34.51; H, 6.11. Cl, 11.32. Found: C, 34.67; H, 6.11; Cl, 11.30.

[η^3-1-(Benzyloxy)-3-(methyl)-1-(trimethylsilyl)-allyl]palladium Chloride (5e) was prepared with use of the procedure for **5a**: Yield 47% (major/minor = 54/46); mp 155-157 °C dec; IR (KBr) no absorption at 1600-1800 cm^{-1}; ^1H NMR ($CDCl_3$) **5e-major** δ 0.36 (s, 9 H), 1.25 (d, J = 5.6 Hz, 3 H), 3.51 (dq, J = 10.0, 5.6 Hz, 1 H), 4.79 (d, J = 11.2 Hz, 1 H), 4.96 (d, J = 11.2 Hz, 1 H), 5.37 (d, J = 10.0 Hz, 1 H), 7.33 (m, 5H); **5e-minor** δ 0.34 (s, 9 H), 1.23 (d, J = 5.6 Hz, 3 H), 3.51 (dq, J = 10.0, 5.1 Hz, 1 H), 4.77 (d, J = 11.0 Hz, 1 H), 4.94 (d, J = 11.0 Hz, 1 H), 5.37 (d, J = 10.0 Hz, 1 H), 7.33 (m, 5 H) . Anal. Calcd for $C_{14}H_{21}OClPdSi$: C, 44.81 ; H, 5.64. Found: C, 45.45; H, 5.63 .

Reaction of 2a with a Stoichiometric Amount of HCl. Under an atmosphere of argon, 109 mg (1 mmol) of

Me_3SiCl was added to a suspension of 285 mg (1 mmol) of **2a** in 10 mL of anhydrous MeOH and the reaction mixture was stirred for 24 h at 25 °C. The reaction mixture was filtered and the filtrate was concentrated in vacuo (5 mmHg). The concentrate was separated with use of column (Florisil, 15 mm i.d. x 100 mm length, CH_2Cl_2). Yellow fractions were concentrated under reduced pressure (1 mmHg) to give crude **5a** in 32% NMR yield.

Reaction of 1a with $PdCl_2(PhCN)_2$ in CD_3OH. Preparation of 9. The solvent in preparation of **5a** was changed from CH_3OH to CD_3OH. The complex **9** was obtained in 65% isolated yield.

Reaction of 2a with a catalytic amount of HCl. Preparation of [η^3-1-(Methoxy)-3-(methoxymethyl)-1-(dimethylphenylsilyl)allyl]palladium Chloride (8). Under an atmosphere of argon, 17 mg (0.16 mmol) of Me_3SiCl was added to a suspension of 227 mg (0.8 mmol) of **2a** in 4 mL of anhydrous MeOH and the reaction mixture stirred for 12 h at 25 °C to generate yellow precipitates. The reaction mixture was filtered and the yellow solids were dissolved in CH_2Cl_2. This solution was concentrated in vacuo to give yellow oily solids. The oily solids were separated with use of a column (Florisil, 15 mm i.d. x 100 mm length, CH_2Cl_2). Yellow fractions were concentrated in vacuo (1 mmHg) to give **8** (129 mg) in 52% isolated yield: mp 128-130 °C dec; IR

(KBr) no absorption at 1600-1800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.34 (s, 9 H), 3.37 (m, 2 H), 3.38 (s, 3 H), 3.56 (s, 3 H), 3.59 (m, 1 H), 5.42 (d, J = 10.3 Hz, 1 H). The peaks at δ 0.34, 3.38, and 3.56 split into three peaks (δ 0.281, 0.303, 0.323; 3.366, 3.385, 3.404; 3.504, 3.541, 3.572), respectively, at -50 °C. Anal. Calcd for $C_9H_{19}O_2ClPdSi$: C, 32.84; H, 5.82; Cl, 10.77. Found: C, 32.80; H, 5.78; Cl, 10.66. The MeOH filtrate was concentrated in vacuo (5 mmHg) and the residue was separated with use of column (Florisil, 15 mm i.d. x 100 mm length, CH_2Cl_2). Yellow fractions were concentrated to give a mixture of **5a** (11%) and **3** (8%).

Transformation of 8 into 5a. Under an atmosphere of argon, 3.0 mg (0.028 mmol) of trimethyl silyl chloride was added to a suspension of 9.1 mg (0.028 mmol) of **8** in 0.4 mL of anhydrous MeOH. After 12 h at 25 °C, the reaction mixture was evaporated under reduced pressure (5 mmHg) and the residue was separated with use of a column chromatography (Florisil, 8 mm i.d. x 70 mm length, CH_2Cl_2). Yellow fractions were concentrated to give **5a** in 27% isolated yield.

Transformation of 8 into 5d. Under an atmosphere of argon, 94.1 mg (0.86 mmol) of trimethyl silyl chloride was added to a suspension of 283 mg (0.86 mmol) of **8** in 5 mL of anhydrous EtOH and the mixture was stirred for 12 h at 25 °C. The reaction mixture was concentrated in vacuo

(5 mmHg) and the concentrate was separated with use of a column chromatography (Florisil, 15 mm i.d. x 100 mm length, CH_2Cl_2). Red fractions were concentrated in vacuo (5 mmHg) to give red oily solids, which were washed with three 3 mL portions of *n*-hexane to give **5d** in 11% isolated yield.

Trapping of the Vinylketene Intermediate with MeOH. Under an atmosphere of argon, 113 mg (0.4 mmol) of **2a**, 153 mg (0.4 mmol) of $PdCl_2(PhCN)_2$, and 30 mg (0.4 mmol) of Li_2CO_3 were suspended in 2 mL of anhydrous MeOH. After 12 h, the reaction mixture was filtered and the filtrate was concentrated in vacuo (5 mmHg). The residue was dissolved in CH_2Cl_2 and dried over anhydrous magnesium sulfate. The drying agent was filtered out and the filtrate was concentrated in vacuo (1 mmHg) to give **3** in 52% isolated yield.

3-4 References and notes

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Chapter 4

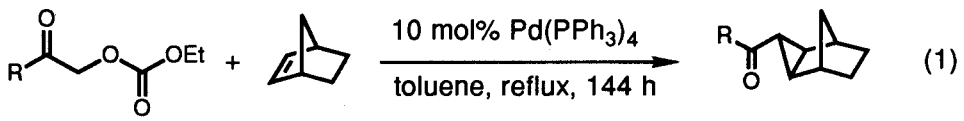
Palladium-Catalyzed Reactions of Ketone α-Carbonates with Norbornenes. An Unusual Cyclopropanation

4-1 Introduction

The chemistry of (oxa-π-allyl)palladium has been thoroughly investigated.[1] Most (oxa-π-allyl)palladium species have been generated by transmetallation of enol silyl ethers with a Pd(II) complex.[1b] However, only scattered examples of direct oxidative addition to Pd(0) species of bonds α to a carbonyl leading to the formation of (oxa-π-allyl)palladium complexes have been reported.[2] To the best of our knowledge, such oxidative additions are limited to a few cases: Palladium(0)-catalyzed carbonylation of α-halo ketones,[3] Pd(0)-catalyzed synthesis of pyrrolidines using an intramolecular cyclization of an α-bromo ester,[4] and conversions of α,β-epoxy ketones to 1,3-diketones[5a] and β-hydroxy ketones.[5b] I have been interested in the formation of carbon-carbon bonds via (oxa-π-allyl)palladium intermediates which are obtained by oxidative addition of ketone α-carbonates to Pd(0) complexes followed by decarboxylation. I wish to report here the unusual palladium catalyzed cyclopropanation mediated by (oxa-π-allyl)palladium.

4-2 Results and Discussion

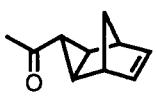
When acetonyl ethyl carbonate (**1a**)[6] reacted with norbornene in the presence of 10 mol % $Pd(PPh_3)_4$ in toluene at reflux temperature, *exo*-3-acetyltricyclo[3.2.1.$0^{2,4}$]octane (**2a**, 90%, GC yield) was obtained (eq 1).



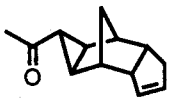
1a: R = CH_3 **2a** 90 %
1b: R = OEt **2b** -

Similarly, the carbonate **1a** reacted with other norbornenes to give the corresponding cyclopropanation products in good yields. When the reaction was carried out in DMF, the rate of the reaction was significantly accelerated. Typical results are listed in Table I.

Table I. Reaction of **1a** with Norbornenes

norbornene	solvent	time, h	product	yield,[a] %
	toluene	144		90 (74)
	DMF	7	**2a**	99
	toluene	111		81 (69)[b]
	DMF	11	**3a**	52[b]

(to be continued)

norbornene	solvent	time, h	product	yield,[a] %
	toluene	90		79 (68)
	DMF	10	**4a**	99

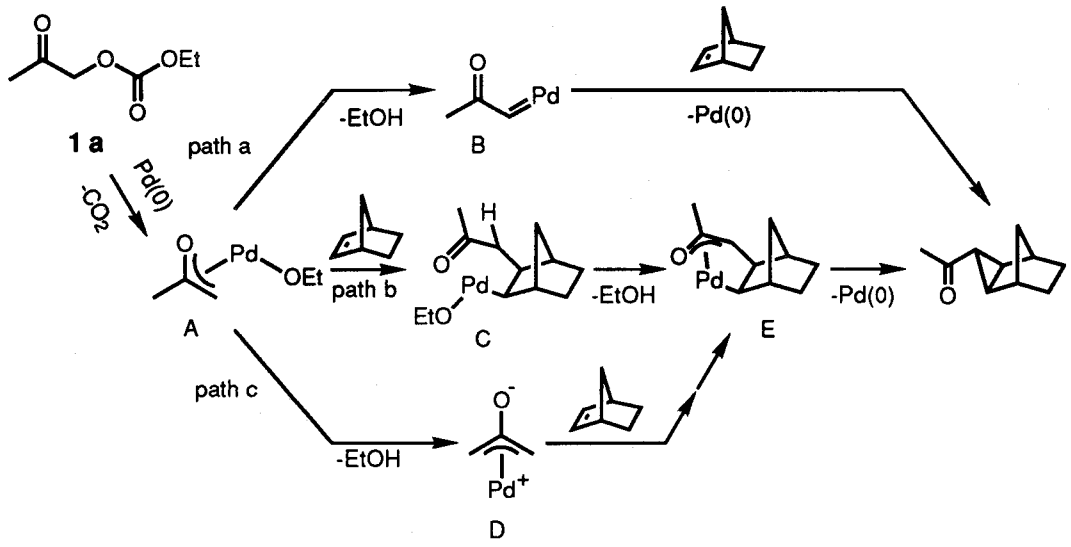
Reaction conditions : carbonate **1a** (1 mmol), norbornene (10 mmol), $Pd(PPh_3)_4$ (0.1 mmol), solvent (3 mL), bath temp. 120 °C.
[a]GC yield. Isolated yields are in parentheses.
[b]Norbornadiene (3 mmol).

The use of excess norbornene relative to carbonate **1a** was required to obtain high yields. A carbonate of ethyl acetate, **1b**,[7] did not react with norbornene under the same reaction conditions.

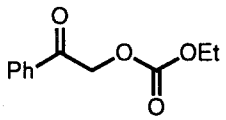
Scheme I shows plausible paths for the formation of the cyclopropane. First, oxidative addition of **1a** followed by decarboxylation affords (oxa-π-allyl)palladium A. In path a, an ethoxy group abstracts a proton α to palladium to generate α-ketocarbene palladium B, which can be expected to react with various olefins.[8] However, carbonate **1a** reacted only with norbornene derivatives to give cyclopropanated products.[9] Thus path a does not seem likely. In path c, proton abstraction from a methyl group leads to formation of oxatrimethylenemethane palladium D (oxatrimethylene-methane = OTMM), which reacts with norbornene to give a cyclopropane through an intermediate E. The intermediacy of E has been postulated in the reaction of OTMM palladium species with norbornene giving the same product.[10] In path b, the

intermediate A adds to norbornene to give an intermediate C, in which proton abstraction at the γ-position leads to the formation of E, releasing ethanol.

Scheme I.



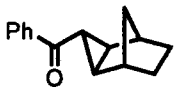
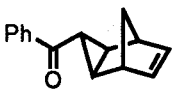
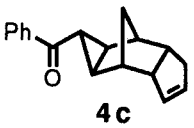
The reactions of phenacyl ethyl carbonate **1c** with norbornenes were examined (Table II). This carbonate also



1c

underwent cyclopropanation with norbornenes to give **2c**, **3c**, and **4c**. This observation ruled out path c, since the reaction of **1c** with the Pd(0) complex cannot give OTMMpalladium. As a consequence, path b is the most likely course of this cyclopropanation reaction. The formation of a byproduct, acetophenone, might have decreased the yield of the cyclopropanated product.

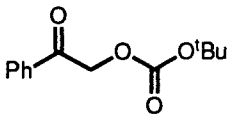
Table II. Reaction of **1c**, **1d**, and **1e** with Norbornenes

carbonate	norbornene	solvent	time, h	product	yield,[a] %
1c		toluene	48	 **2c**	58 (56)
		DMF	1		82 (82)
		toluene	24	 **3c**	33[b] (29)
		DMF	3		43[b]
		toluene	16	 **4c**	31 (29)
		DMF	1		35
1d		toluene	48	**2c**	52 (40)
		DMF	5		(55)
1e		toluene	42	**2c**	14
		DMF	21		16

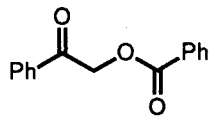
Reaction conditions : carbonate **1a** (1 mmol), norbornene (10 mmol), $Pd(PPh_3)_4$ (0.1 mmol), solvent (3 mL), bath temp. 120 °C. [a] GC yield. Isolated yields are in parentheses. [b]Norbornadiene (3 mmol)

A considerable amount (18-67% yields) of acetophenone has also been obtained, probably consuming

the common intermediate F which otherwise leads to the cyclopropanation product[11].

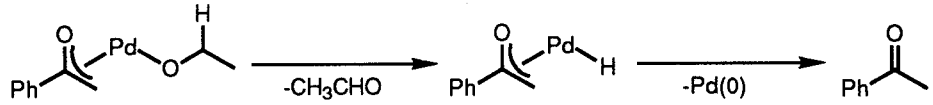


1d



1e

To suppress the formation of acetophenone, the reaction of **1d** and **1e**, which have no β-hydrogen, with norbornene were attempted, but was generated. We can not propose a suitable reaction path to account for the formation of acetophenone. Thus, further studies are required.



F

We have described here an unusual cyclopropanation in the palladium-catalyzed reaction of ketone α-carbonates with norbornene. This reaction proceeds via the (oxa-π-allyl)palladium intermediate. More detailed studies on the scope and usefulness of this (oxa-π-allyl)palladium species are in progress.

4-3 Experimental Section

General Procedures. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded in $CDCl_3$ with a reference to TMS. Melting points are uncorrected. IR spectra were recorded as KBr pellets. GLC analysis (25 m x 0.2 mm CBP1-M25-025 capillary column) were performed with a flame ionization detector and N_2 carrier gas.

Ethoxycarbonyloxyacetone (1a). To a solution of 7.41 g (100 mmol) of α-hydroxyacetone in 50 mL of pyridine was added dropwise 17.6 g (163 mmol) of ethyl chloroformate at room temperature and the mixture was stirred for 1 h. The reaction mixture was poured into 300 mL of hexane, and the precipitated pyridinium chloride was filtered off. The filtrate was evaporated in vacuo and the residue was distilled (52-54 °C/0.8 mmHg, 58%).

Ethyl Ethoxycarbonyloxyacetate(1b). To a solution of 13.7 g (131 mmol) of ethyl hydroxyacetate in 100 mL of dry Et_2O was added dropwise 14.3 g (131 mmol) of ethyl chloroformate at 0 °C under a nitrogen atmosphere. The reaction mixture was washed with 100 mL of 9% aqueous HCl solution, 50 mL of saturated $NaHCO_3$, and 50 mL of brine. The organic layer was dried over $MgSO_4$ for 2 h and evaporated. The residue was distilled (89-93 °C /7 mmHg, yield 63%).

Ethoxycarbolyloxyacetophenone (1c). To a solution of 1.40 g (10 mmol) of α-hydroxyacetophenone in 20 mL of dry pyridine was added dropwise 2.3 g (21 mmol) of ethyl chloroformate at room temperature. The mixture was stirred for 2 h and 20 mL of hexane was added. The precipitate were filtered and the filtrate was concentrated. The residue was distiled to give **1c** (119-121 °C/3 mmHg, Yield 89%). mp 46-47 °C; IR (KBr) 1750 (carbonate), 1706 (ketone) cm^{-1}, ^1H NMR ($CDCl_3$) δ 1.36 (t,

J = 7.1 Hz, 3 H), 4,28 (q, J = 7.1 Hz, 2 H), 5.36 (s, 2 H), 7.50 (dd, J = 7.8, 7.3 Hz, 2 H), 7.62 (t, J = 7.3 Hz, 1 H), 7.92 (d, J = 7.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 64.7, 68.5, 127.7, 128.9, 133.9, 133.9, 154.8, 191.8. Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.46; H, 5.81. Found: C, 63.42; H, 5.74.

***t*-Butoxycarbonyloxyacetophenone(1d).** Under a nitrogen atmosphere, a solution of 0.467 g (4.16 mmol) of *t*-BuOK and 0.463 g (6.24 mmol) of *t*-BuOH in 15 mL of dry THF was added dropwise to a suspension of 1.686 g (10.4 mmol) of carbonyl diimidazole in 10 mL of dry THF, and the mixture was stirred overnight. To the reaction mixture was added a solution of 1.415 g (10.4 mmol) of α-hydroxyacetophenone at 0 °C. The mixture was stirred for 2 h and concentrated. The residue was washed with 30 mL of H_2O and extracted with four 20 mL portions of $CHCl_3$. The organic layer was dried over $MgSO_4$ and concentrated. The residue was separated with use of a column chromatography (silica gel 100-200 mesh, hexane/Et_2O = 1/1, R_f=0.34, yield 40%): mp 44-46 °C; IR (KBr) 1752 (carbonate), 1710 (ketone) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.53 (s, 9 H), 5.29 (s, 2 H), 7.49 (dd, J = 7.6, 8.1 Hz, 2 H), 7.58 (t, J = 7.6 Hz, 1 H), 7.90 (d, J = 8.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 27.7, 67.9, 83.0, 127.7, 128.8, 133.8, 134.1, 153.1, 192.2. Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 66.14; H, 6.64.

Phenoxycarbonyloxyacetophenone(1e). Under a nitrogen atmosphere, to a solution of 0.88 g (6.47 mmol) of α-hydroxyacetophenone in 15 mL of dry pyridine was added dropwise 2.0 g (2.5 mL, 12.8 mmol) of phenyl chloroformate at 25 °C. The reaction mixture was stirred for 2 h and appropriate amounts of hexane was added. The precipitate were filtered and the filtrate was concentrated. The residue was purified with use of a column chromatography (silica gel 100-200 mesh, hexane/Et_2O = 1/1, R_f = 0.37) to give **1e** in 100% isolated yield: mp 64-66 °C; IR (KBr) 1715, 1775 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.46 (s, 2 H), 7.24 (d, *J* = 8.4 Hz, 2 H), 7.27 (d, *J* = 7.3 Hz, 1H), 7.42 (m, 2 H), 7.53 (dd, *J* = 7.3, 7.8 Hz, 2 H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 69.09, 120.95, 126.14, 127.73, 128.94, 129.47, 133.84, 134.10, 151.12, 153.42, 191.23.

Typical Procedure for Reaction of 1c with Norbornene. Under a nitrogen atmosphere, 206 mg (0.989 mmol) of carbonate **1c**, 942 mg (9.89 mmol) of norbornene, and 116 mg (0.1 mmol) of $Pd(PPh_3)_4$ were dissolved in 3 mL of dry DMF. The solution was stirred at 120 °C (bath temperature) for 1 h and concentrated in vacuo. The residue was purified with use of a column chromatography (silica gel 100-200 mesh, hexane/Et_2O = 5/1) to give **2c** (82%) and acetophenone (16%).

3-Benzoyltricyclo[3.2.1.$0^{2,4}$]octane(2c). mp 69-71 °C; IR (KBr) 1654(carbonyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.81 (d, *J* = 10.8 Hz, 1 H), 1.13 (dt, *J* = 10.8, 1.9 Hz, 1 H), 1.33-1.41 (m, 1 H), 1.48-1.56 (m, 1 H), 1.62 (d, *J* = 2.4 Hz, 2 H), 2.44 (bs, 2 H), 2.61 (t, *J* = 2.4 Hz, 1 H), 7.45 (dd, *J* = 6.8, 7.3 Hz, 2 H), 7.54 (t, *J* = 7.3 Hz, 1 H), 7.95 (d, *J* = 6.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.1, 28.7, 29.1, 30.0, 36.2, 127.8, 128.4, 132.4, 138.4, 200.3. Anal. Calcd for $C_{15}H_{16}O$: C,84.87; H, 7.60. Found: C, 84.78; H, 7.64.

3-Benzoyltricyclo[3.2.1.$0^{2,4}$]-6-octene(3c). mp 85-85 °C; IR (KBr) 1660 (carbonyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.13 (d, *J* = 9.5 Hz, 1 H), 1.36 (dd, *J* = 9.5, 2.4 Hz, 1 H), 1.89 (d, *J* = 2.4 Hz, 2 H), 3.00 (bs, 2 H), 3.60 (t, *J* = 2.4 Hz, 1 H), 6.47 (t, *J* = 1.7 Hz, 2 H), 7.46 (dd, *J* = 7.0, 7.3 Hz, 2 H), 7.56 (t, *J* = 7.3 Hz, 1 H), 7.98 (d, *J* = 7.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 35.2, 36.9, 40.4, 42.2, 128.0, 132.6, 137.8, 140.9, 197.3. Anal, Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.46; H, 6.71.

9-Benzoyltetracyclo[5.3.1.$0^{2,6}$.$0^{8,10}$]-3-undecene (4c). mp 114-116 °C; IR (KBr) 1660 (carbonyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (d, *J* = 10.7 Hz, 1 H), 1.25 (d, *J* = 10.7 Hz, 1 H), 1.47 (d, *J* = 7.1 Hz, 1 H), 1.76 (d, *J* = 7.1 Hz, 1 H), 2.19-2.31 (m, 1 H), 2.35-2.40 (m 1 H), 2.41-2.46 (m, 1 H), 2.51-2.54 (m, 1 H), 2.57-2.67 (m, 1 H), 2.69 (t, *J* = 2.7 Hz, 1 H), 3.12-3.21 (m, 1 H), 5.55-

5.59 (m, 1 H), 5.75-5.79 (m, 1 H), 7.44 (dd, J = 7.3, 7.0 Hz, 2 H), 7.53 (t, J = 7.3 Hz, 1 H), 7.94 (d, J = 7.0, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.3, 25.0, 28.1, 31.5, 31.9, 38.6, 39.9, 43.0, 54.7, 127.8, 128.3, 130.0, 132.4, 132.9, 138.5, 200.3. Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.13; H, 7.34.

4-4 References and Notes

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(2) It has been reported that oxidative addition of allyl enol carbonates to Pd(0) followed by decarboxylation has led to the formation of (π-allyl)palladium enolate (oxa-π-allyl). See ref 1a.

(3) Stille, J. K,; Wong, P. K. *J. Org. Chem.* **1975**, *40*, 532.

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Commun. **1991**, 1559. Sasaki, Y. *Tetrahedron Lett.* **1986**, *27*, 1573.

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(10) Trost, B. M.; Schneider, S. *J. Am. Chem. Soc.* **1989**, *111*, 4430. Trost, B. M.; Urabe, H. *Tetrahedron Lett.* **1990**, *31*, 615. It has been also reported that azatrimethylenemethanepalladium reacted with norbornene to bring about a similar cyclopropanation. Ohe, K.; Ishihara, T.; Chatani, N.; Murai, S. *J. Am. Chem. Soc.* **1990**, *112*, 9646

(11) The β-elimination from the intermediate F may lead to the formation of an (oxa-π-allyl)palladium hydride. See for a related reaction: Tsuji,J.; Minami, I.; Shimizu, I. *Tetrahedron Lett.* **1984**, *25*, 279.

Conclusion

In this thesis, the new aspects of synthesis and reactivity of (η^3-allyl)palladium complexes have been studied. The results investigated in this thesis are summarized as follows.

In Chapter 1, the reaction of allyl silane with palladium(II) complexes in the presence of triethylamine has described. While the reaction of allyltrimethylsilane with $PdCl_2(CH_3CN)_2$ gave (η^3-allyl)palladium chloride by desilylation, addition of Et_3N changed the reaction course completely leading to a different product [η^3-(1-trimethylsilyl)allyl]palladium chloride by deprotonation.

In Chapter 2, new type of (η^3-allyl)palladium complexes, [η^3-1-(formyl)allyl]palladium chloride and [η^3-1-(dimethoxymethyl)allyl]palladium chloride, have been efficiently synthesized. The latter (η^3-allyl)palladium complex reacted with enol silyl ether to give aldol product in which (η^3-allyl)palladium moiety remained intact.

In Chapter 3, reaction of the 1-silyl dienol silyl ethers with Pd(II) salts has been described. This reaction gave various η^3-allylpalladium complexes depending on the type of Pd(II) salts , solvents, and the acidity of the medium. Treatment of 1-silyl dienol silyl ethers with Li_2PdCl_4 in the presence of Li_2CO_3 in MeOH resulted in simple transmetallation to give the [η^3-1-

(silylcarbonyl)allyl]palladium chloride. The other (η^3-allyl)palladium complexes generated via the versatile complex [η^3-1-(silylcarbonyl)allyl]palladium chloride. And possible reaction sequences connecting all of these η^3-allyl complexes were proposed.

In Chapter 4, the palladium-catalyzed reaction of ketone α-carbonates with norbornenes has been described. In the presence of a palladium(0) catalyst, ketone α-carbonates react with norbornene to give a cyclopropane derivative via an oxa-π-allylpalladium intermediate.