Interaction of Palladium(0) Complexes with Allylic Acetates, Allyl Ethers, Allyl Phenyl Chalcogenides, Allylic Alcohols, and Allylamines. Oxidative Addition, Condensation, Disproportionation, and π-Complex Formation

Takakazu Yamamoto,* Mitsuru Akimoto, Osamu Saito, and Akio Yamamoto

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

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Allyl acetate and allyl aryl ether react with $Pd(PCy_3)_2$ (1) at room temperature to afford $Pd(\eta^3\text{-}C_3H_5)(OY)(PCy_3)$ (Y = acetyl (3), *p*-cyanophenyl (8)) and $[Cy_3PCH{=}CHCH_3][OY]$. The reaction of 1 with $CH_2{=}CHCD_2OAc$ at room temperature leads to the formation of a 1:1 mixture of *cis*- and *trans*-$Pd(\eta^3\text{-}CH_2CHCD_2)(OAc)(PCy_3)$ accompanied by a 1,3-shift of $CH_2{=}CHCD_2OAc$. Reactions of allyl phenyl sulfide and allyl phenyl selenide with 1 and $Pd(P\text{-}t\text{-}Bu_3)_2$ (2) afford dinuclear $Pd_2(\mu\text{-}C_3H_5)(\mu\text{-}ZPh)L_2$ (Z = S, Se) complexes. Reactions of allyl alcohol and 1-methylallyl alcohol with 1 yield Pd(diallyl ether)(PCy_3) and Pd(*meso*-bis(methylallyl) ether)(PCy_3), respectively, and mixtures of diallylic ethers. Reactions of crotyl alcohol and 2-methylallyl alcohol with 1 by dismutation give the corresponding aldehyde and alkene; in the case of crotyl alcohol, Pd(crotonaldehyde)$(PCy_3)_2$ has been isolated. The reaction of 1 with *N*-allyltriethylamine bromide affords $Pd(\eta^3\text{-}C_3H_5)(Br)(PCy_3)$, whereas the reaction with *N*-allylaniline affords Pd(*N*-allylaniline)$(PCy_3)_2$. These Pd complexes are not ionic in solutions. Variable-temperature ^1H NMR spectra of 3 show fluxional properties of the η^3-allyl ligand at room temperature, whereas 8 was found to be rigid. Complexes 3 and 8 react with nucleophiles to afford the corresponding allylated products. Complexes 3 and 8 have the propensity to form binuclear $Pd_2(\mu\text{-}C_3H_5)(\mu\text{-}OY)(PCy_3)_2$ complexes in reactions with nucleophiles, PCy_3, and 1 and in their thermolysis reactions.

Oxidative addition of allylic compounds[1] having allylic halogen,[1,2] oxygen,[3] chalcogen (S, Se),[4] and nitrogen[5] bonds with Pd(0) complexes is utilized in various types of homogeneous catalytic reactions including allylation of nucleophiles,[1,3a,f-k] carbonylation of allylic compounds,[1d,3e] formation of dienes from allylic phenolates or acetates,[3c] oxidation of alcohols,[3l] and reduction of allylic alcohols.[3m,t] Among the oxidative addition reactions of the allylic compounds, that of allylic compounds having an allylic halogen bond (allylic halogen compounds) has been well-studied. Isolation of $Pd(\eta^3\text{-allyl})(halogen)L_n$-type complex from the reaction systems is reported,[2] and it is established that the $Pd(\eta^3\text{-allyl})(halogen)L_n$-type complexes allylates nucleophiles.[6a,b,d,e,g,h] A theoretical explanation on the allylation of nucleophiles by $Pd(\eta^3\text{-allyl})(halogen)L_n$ is also given.[6c]

The oxidative addition of compounds having an allylic oxygen bond (allylic oxygen compounds), on the other hand, has been less explored compared with the oxidative addition of allylic halogen compounds in spite of very wide use of the allylic oxygen compounds in syntheses.[3] In this paper we report (i) the isolation of Pd complexes with allylic acetate, allyl phenolates, and allylic alcohols and (ii) the properties and reactivities of the isolated complexes. Extension of the reactions by using allyl phenyl chalcogenides and allylamines is also reported.

In this research we first attempted isolation of the $(\eta^3\text{-allyl})(acetato)$palladium-type complex from a mixture of allyl acetate and coordinatively saturated $Pd(PPh_3)_4$.[7] However, no apparent change was observed on mixing $Pd(PPh_3)_4$ with allyl acetate even at elevated temperature (80 °C), though the palladium complex was found to

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Table I. Products of Reactions of Allylic O, S, Se, and N Compounds with PdL_2 (L = PCy_3, P-*t*-Bu_3)

expt	reactant (mol/PdL_2)	Pd complex	solv	temp, °C	time, h	products [% yield/PdL_2]
1	CH_2=$CHCH_2OCOCH_3$ (ex)[a]	1[b]	none	rt[d]	12	$Pd(\eta^3$-$C_3H_5)(OCOCH_3)L$ (**3**) [43], $[PCy_3(CH$=$CHCH_3)][OCOCH_3]$ (**4**) [43]
2	CH_2=$C(CH_3)CH_2OCOCH_3$ (ex)	1	none	rt	36	$Pd(\eta^3$-$CH_2C(CH_3)CH_2)(OCOCH_3)L$ (**5**) [60]
3	CH_2=$CHCH_2OC_6H_5$ (2.7)	1	toluene	rt	24	$Pd(\eta^3$-$C_3H_5)(OC_6H_5)L$ (**6**), $[PCy_3(CH$=$CHCH_3)][OC_6H_5]$ (**7**) [58]
4	CH_2=$CHCH_2OC_6H_4$-*p*-CN (2.7)	1	toluene	rt	48	$[Pd(\eta^3$-$C_3H_5)(OC_6H_4$-*p*-$CN)L$ (**8**) [47] $[PCy_3(CH$=$CHCH_3)](OC_6H_4$-*p*-CN) (**9**) [100]
5	CH_2=$CHCH_2SC_6H_5$ (2.8)	1	toluene	rt	0.2	$Pd_2(\mu$-$C_3H_5)(\mu$-$SC_6H_5)L_2$ (**10a**) [85]
6	CH_2=$CHCH_2SC_6H_5$ (1.4)	2[b]	benzene	rt	0.5	$Pd_2(\mu$-$C_3H_5)(\mu$-$SC_6H_5)L_2$ (**10b**) [40]
7	CH_2=$CHCH_2SeC_6H_5$ (1.0)	1	toluene	rt	0.2	$Pd_2(\mu$-$C_3H_5)(\mu$-$SeC_6H_5)L_2$ (**11a**) [55]
8	CH_2=$CHCH_2SeC_6H_5$ (1.4)	2	benzene	rt	2	$Pd_2(\mu$-$C_3H_5)(\mu$-$SeC_6H_5)L_2$ (**11b**) [20]
9	CH_2=$CHCH_2OH$ (ex)	1	none	30	96	Pd(diallyl ether)L (**12**) [61], diallyl ether [530], H_2O[c]
10	CH_2=$CHCH(CH_3)OH$ (ex)	1	none	70	8	Pd(*meso*-bis(1-methylallyl) ether) L (**13**) [58], *meso*-bis(1-methylallyl) ether [72], *dl*-bis(1-methylallyl) ether [180], H_2O,[c] 1-methylallyl crotyl ether [28], butadiene [220]
11	CH_3CH=$CHCH_2OH$ (ex)	1	none	70	18	*trans*-C_4H_8 [4], *cis*-C_4H_8 [2], $Pd(CH_3CH$=$CHCHO)L_2$ (**14**) [47], 1-C_4H_8 [94], 1-methylallyl crotyl ether [175], dicrotyl ether [22], H_2O [60]
12	CH_2=$C(CH_3)CH_2OH$ (ex)	1	none	70	4	Pd metal, methacrolein [230], isobutene [360], bis(2-methylallyl) ether [440], H_2O[c]
13	CH_2=$CHCH_2OH$ (ex) + C_2H_5OH (ex)	1	none	rt	72	diallyl ether [280], allyl ethyl ether [150]
14	$[CH_2$=$CHCH_2NEt_3]Br$ (3.0)	1	THF	rt	24	$Pd(\eta^3$-$C_3H_5)(Br)L$ (**15**) [74]
15	CH_2=$CHCH_2NHC_6H_5$ (2.9)	1	toluene	70	2	Pd(*N*-allylaniline)L_2 (**16**) [85]

[a] ex = excess (10–100 mol/PdL_2). [b] 1 = $Pd(PCy_3)_2$ and 2 = $Pd(P$-*t*-$Bu_3)_2$. [c] Formation of H_2O was confirmed by GLC, but its amount was not measured. [d] rt = room temperature.

catalyze the 1,3-shift of allyl-d_2 acetate. A reaction of Pd(ethylene)$(PPh_3)_2$ with allyl acetate gave no oxidative addition product, either. In contrast to the reactions of $Pd(PPh_3)_4$ and Pd(ethylene)$(PPh_3)_2$, that of $Pd(PCy_3)_2$ (PCy_3 = tricyclohexylphosphine)[8] with allyl acetate proceeds smoothly to afford $Pd(\eta^3$-$C_3H_5)(OAc)(PCy_3)$. Coordinative unsaturation of $Pd(PCy_3)_2$ and high basicity of PCy_3 seem to facilitate the oxidative addition. Because of this observation, our present research is mostly concerned with the reactions of the allylic compounds with $Pd(PCy_3)_2$ and its analogue, $Pd(P$-*t*-$Bu_3)_2$[8] (P-*t*-Bu_3 = tri-*tert*-butylphosphine). A part of the results given in this paper has been reported in communication form.[9]

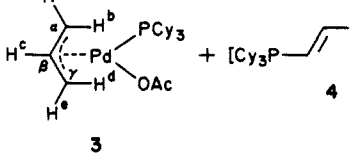
Results and Discussion

Table I summarizes results of the reactions of allylic carboxylates, allylic ethers, allyl phenyl chalcogenides, and allylamines with $Pd(PCy_3)_2$ (**1**) and $Pd(P$-*t*-$Bu_3)_2$ (**2**).

Allylic Acetates The reaction of **1** with allyl acetate proceeds smoothly at room temperature to give $Pd(\eta^3$-$C_3H_5)(OAc)(PCy_3)$ (**3**) and $[(E)$-Cy_3PCH=$CHCH_3]^+[OAc]^-$ (**4**) (experiment 1 in Table I). Compound **3** and **4** can be separated due to differences in their solubility in solutions.

$$Pd(PCy_3)_2 + CH_2{=}CHCH_2OAc \xrightarrow{\text{room temp, 12 h}} \mathbf{3} + [Cy_3P{-}\text{allyl}]^+[OAc]^- \quad (1)$$

1



3 + [Cy3P-allyl]+[OAc]- (1)

4

Formation of a dinuclear complex, $(PCy_3)_2Pd_2(\mu$-$C_3H_5)(\mu$-OAc) (**17**), which is considered to be produced through a coupling reaction between **3** and **1** (vide infra), sometimes accompanies reaction 1, depending on reaction conditions. Compounds **3** and **4** can be synthesized through different reaction pathways, eq 2 and 3, the fact

$$[Pd(\eta^3\text{-}C_3H_5)(OAc)]_2 + PCy_3 \rightarrow \mathbf{3} \quad (2)$$

$$PCy_3 + CH_2CHCH_2Br \rightarrow [Cy_3PCH_2CH{=}CH_2]^+Br^- \xrightarrow{+AgOAc} \mathbf{4} \quad (3)$$

also supporting the formulation of the compounds. Concerning reaction 3, it is known that the AcO^- ion catalyzes isomerization of $[R_3PCH_2CH$=$CH_2]^+$ to $[R_3PCH$=$CHCH_3]^+$.[10] Table II summarizes analytical, IR, and NMR data of **3**, **4**, and other compounds reported in this paper.

The IR spectrum of **3** resembles that of its Ni analogue, $Ni(\eta^3$-$C_3H_5)(OAc)(PCy_3)_2$,[11a] showing a ν(C=O) band at 1600 cm^{-1}. The variable-temperature ^1H NMR spectrum of **3** reveals the fluxional motion of the η^3-allyl ligand at higher temperatures. At lower temperature (−71 °C or below) the ^1H NMR spectrum shows an ABCDX spin pattern characteristic of the η^3-allyl ligand,[12] but at 25 °C the two doublets of H^a and H^b are averaged to give rise to a doublet (J = 9 Hz) at δ 2.80 due to rapid movement

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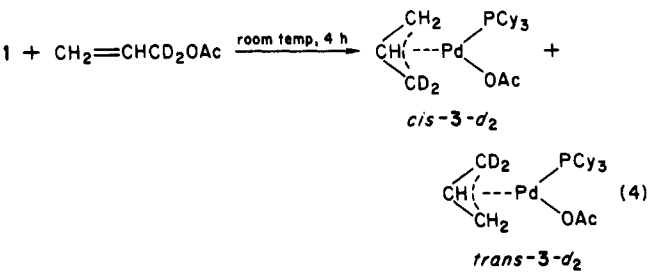
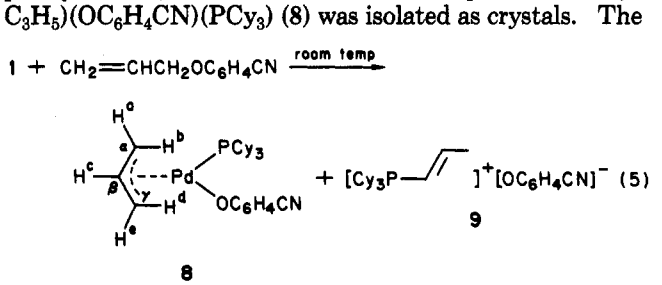
of the allyl ligand via η^3-allyl $\rightleftharpoons$ η^1-allyl isomerization.[12c,d,g] The ^{13}C NMR spectrum of **3** shows allylic C^α–C^γ signals[12e,f] and OAc signals at reasonable positions. The reaction of 2-methylallyl acetate with **1** also causes similar C–O bond cleavage as shown in Table I, giving $Pd(\eta^3\text{-}CH_2C(CH_3)CH_2)(OAc)(PCy_3)$ (**5**) (experiment 2). The variable-temperature ^1H NMR spectrum of **5** also reveals the fluxional motion of the 2-methylallyl ligand at room temperature; the two peaks at δ 2.18 and 2.76 observed at −50 °C (Table II) are averaged to give one broad peak at δ 2.5. A similar averaging phenomenon of two allylic ^1H signals of $Pd(\eta^3\text{-}CH_2C(CH_3)CH_2)(OAc)(PPh_3)$ has been reported.[13]

Employment of CH_2CHCD_2OAc in the reaction with **1** at room temperature affords a mixture of cis and trans isomers of $Pd(\eta^3\text{-}CH_2CHCD_2)(OAc)(PCy_3)$ and a mixture of $[Cy_3PCH{=}CHCHD_2]^+[OAc]^-$ and $[Cy_3PCD{=}CHCH_2D]$ as revealed by ^1H NMR analysis of the product.

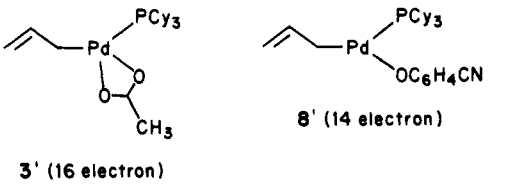


The allyl acetate remaining after the reaction was found to be a mixture of almost equal amounts of $CH_2{=}CHCD_2OAc$ and $CD_2{=}CHCH_2OAc$. Formation of the mixture of the cis and trans isomers suggests that initially formed oxidative addition product is isomerized. The oxidative addition of allyl acetate may occur with inversion of configuration at carbon, such inversion having been observed for a reaction system.[3r]

Allyl Ethers. The reaction of allyl phenyl ether with **1** in toluene at room temperature affords $[PCy_3(CH{=}CHCH_3)]^+[OC_6H_5]^-$ (**7**) and a yellow oily palladium compound whose IR spectrum shows a strong ν(CO) band at 1260 cm^{-1} characteristic of transition-metal phenoxides.[11a,14] Analytical data of the palladium compound approximately are consistent with a structure of $Pd(\eta^3\text{-}C_3H_5)(OPh)(PCy_3)$(toluene) (**6**). These facts suggest the occurrence of oxidative addition of allyl phenyl ether to palladium, although isolation of **6** was not feasible due to lack of a suitable solvent for its recrystallization. When allyl *p*-cyanophenyl ether is employed instead of allyl phenyl ether, the oxidative addition product $Pd(\eta^3\text{-}C_3H_5)(OC_6H_4CN)(PCy_3)$ (**8**) was isolated as crystals. The

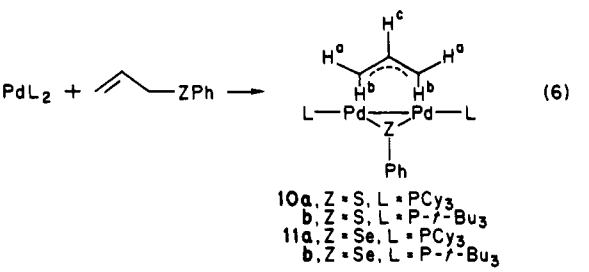


spin–spin coupling pattern of the allylic signals in ^1H NMR of **8** is almost the same as that observed for the acetate complex **3**, but the variable-temperature ^1H NMR spectrum of the allylpalladium cyanophenoxide complex **8** does not show averaging of the H^a and H^b signals even at 60 °C where AX_4 pattern is observed for **3**. The difference in the fluxional behavior between **3** and **8** seems to be attributable to the difference in stability of the intermediate (η^1-allyl)palladium(II) complex. In the case of the acetate complex **3**, coordination of OAc as a bidentate ligand may stabilize the intermediate (η^1-allyl)palladium species by giving a 16-electron complex, **3′**,[12c] whereas the η^1-allyl-type



isomer of **8**, **8′**, has only 14 electrons. When pyridine-d_5 (1 mol/8) is added to the CD_2Cl_2 solution of **8**, the ^1H NMR spectrum of **8** at 25 °C shows a new peak at 2.8 ppm due to the averaging of H^a and H^b peaks, though the other allylic signals (H^c–H^e) are essentially not changed. Coordination of pyridine to **8′** seems to stabilize the η^1-allyl structure, thus facilitating the dynamic movement of the allyl ligand via the η^1–η^3 isomerization. Allyl alkyl ether did not undergo oxidative addition to $Pd(PCy_3)_2$.

Allyl Phenyl Chalcogenides. Reactions of allyl phenyl sulfide and allyl phenyl selenide with **1** and **2** are completed instantly at room temperature (experiments 5–8 in Table I) to yield $Pd_2(\mu\text{-}C_3H_5)(\mu\text{-}SPh)L_2$ (**10**) and $Pd_2(\mu\text{-}C_3H_5)(\mu\text{-}SePh)L_2$ (**11**), respectively. Complexes **10** and



11 appear to be formed by reactions of the initially formed oxidative addition products $Pd(\eta^3\text{-}C_3H_5)(ZPh)L$ with intact PdL_2 or PdL. Attempts to isolate the $Pd(\eta^3\text{-}C_3H_5)(ZPh)L$-type complex failed, possibly due to its high reactivity toward PdL_2 or PdL. The high reactivity of the supposed mononuclear $Pd(\eta^3\text{-}C_3H_5)(ZPh)L$ complex toward PdL_2 or PdL seems to be related to radii of S and Se which may be suitable to make the bridging bond in **10** and **11**. A competition experiment using a mixture of allyl phenyl sulfide and allyl phenyl selenide (45:55 molar ratio) in the reaction with **1** affords **10a** and **11a** in a molar ratio of 40:60, revealing that allyl phenyl sulfide and selenide have almost the same reactivity toward the Pd(0) complex. Complexes **10** and **11** are characterized by elemental analysis and IR and NMR spectroscopy. Assignment of μ-allylic signals in the ^1H NMR spectrum of **10b** has been performed by comparing the ^1H NMR spectrum with those of $Pd_2(\mu\text{-}C_3H_5)(\mu\text{-}OAc)(P\text{-}i\text{-}Pr_3)_2$[15a] and $Pd_2(\mu\text{-}CH_2C(CH_3)CH_2)(\mu\text{-}SPh)(P\text{-}i\text{-}Pr_3)_2$[15b] (P-*i*-$Pr_3$ = triisopropylphosphine), which have been prepared by Werner and his co-workers through a different type of reaction. Although allyl phenyl sulfide and selenide have very high reactivity toward **1** and **2**, they do not show any apparent reactivity toward coordinatively saturated $Pd(PPh_3)_4$.

Allylic Alcohols. Interaction of allylic alcohols with **1** leads to various types of reaction products depending

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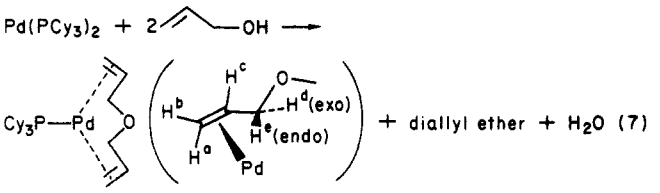
Table II. Analytical, IR, and NMR Data of Compounds 3–17 and 24′ and Electric Conductivities of Solutions Containing the Compounds

compd	mp, °C	anal. found (calcd) C	H	N, Br, or S	IR,[a] cm^{-1}	^{1}H NMR,[b] δ solv	temp, °C	allylic or related H	phosphine	others	^{13}C{^{1}H} or ^{31}P{^{1}H} NMR[c]	EC,[d] μS/cm
3	134–136 dec	57.1 (56.7)	8.9 (8.4)		1600, 1445, 1360, 1315, 995	acetone-d_6	−71	2.40 (1 H, d, H^b),[e] 3.24 (1 H, d, H^e), 3.70 (1 H, dd, H^d), 4.40 (1 H, t, H^a), 5.28 (1 H, m, H^c)	1.1–2.1 (33 H)[e]	1.8 (3 H, s, OAc)[e]	24.0 (OCOCH_3), 45.2 (s, C$^\alpha$), 78.0 (d, 28 Hz, C$^\gamma$), 116.2 (d, 4 Hz, C$^\beta$), 160 (O$COCH_3$)	2.9
								J(H^a–H^c) = 6 Hz, J(H^b–H^c) = 12 Hz, J(H^c–H^d) = 14 Hz J(H^c–H^e) = 8 Hz, J(H^{d}–^{31}P) = 9 Hz, J(H^{e}–^{31}P) = 8 Hz			40.2 (s)[f]	
							25	2.80 (2 H, d, H^a + H^b), 3.68 (1 H, dd, H^d), 4.39 (1 H, t, H^e), 5.30 (1 H, ddt, H^c)	1.1–2.1 (33 H)[e]	1.8 (3 H, s, OAc)[e]		
4	107–109	71.8 (72.6)	11.2 (10.8)		1650, 1280	CD_2Cl_2	25	2.10 (3 H, dt, CH_3), 5.80 (1 H, ddq, =C*H*P), 6.75 (1 H, tq, =C*H*CH_3)	1.1–2.1 (33 H)	1.8 (3 H, s, OAc)	23.6 (OCOCH_3), 28.1 (=CHCH_3), 106.6 (=CHP), 158.9 (=$CHCH_3$), 173.8 (O$COCH_3$)	46.0
5		*h*			1595, 1440, 1355, 1310, 995	CD_2Cl_2	−50	1.80 (3 H, d, 1 Hz, CH_3),[e] 2.18 (1 H, m), 2.76 (1 H, m), 3.44 (1 H, d, 8 Hz), 4.33 (1 H, m)	0.9–2.0 (33 H)[e]	1.8 (3 H, s, OAc)[e]	25.1[f]	
6		*i*			1580, 1470, 1440, 1260, 745							
7	130–131	78.0 (78.2)	10.0 (10.5)		1590, 1490, 1440, 1300	CD_2Cl_2	25	2.14 (3 H, dt, CH_3),[e] 5.82 (1 H, m, =CHP), 6.64 (1 H, m, =C*H*CH_3)	1.2–2.1 (33 H)[e]	6.8–7.4 (5 H, OPh)	30.5 (s)[f]	46.9
8	160–161 dec	61.7 (61.6)	8.1 (7.8)	2.5 (2.6)	2220, 1585, 1490, 1330	CD_2Cl_2	25	2.40 (1 H, d, H^b), 3.20 (1 H, d, H^a), 3.55 (1 H, dd, H^d), 4.46 (1 H, t, H^e), 5.50 (1 H, m)	1.2–2.1 (33 H)	6.50 (2 H, d, 9 Hz, OC_6H_4-CN), 7.23 (2 H, d, 9 Hz, OC_6H_4CN)	47.0 (s)[f]	0.5
								J(H^a–H^c) = 6 Hz, J(H^b–H^c) = 12 Hz, J(H^c–H^d) = 14 Hz J(H^c–H^e) = 8 Hz, J(H^{d}–^{3P}) = 9 Hz, J(H^{e}–^{31}P) = 6 Hz				
9	129–130	76.0 (76.5)	9.0 (9.6)	3.9 (3.2)	2200, 1580, 1510, 1440	CD_2Cl_2	25	2.14 (3 H, dt, CH_3), 5.86 (1 H, m, =CHP), 6.91 (1 H, m, =C*H*CH_3)	1.4–2.6 (33 H)	6.44 (2 H, d, 9 Hz, OC_6H_4-CN), 7.63 (2 H, d, 9 Hz, OC_6H_4CN)	30.6 (s)[f]	46.7
10a	255.5–259.5 dec	57.8 (57.5)	8.6 (8.3)	3.4 (3.5)	1570, 1465, 1440, 510	C_6D_6	25	2.80 (1 H, m, H^c), 3.57 (2 H, m, H^a)		6.9–7.6 (5 H, m, SPh)	47.0 (s)[f]	0.1
								0.88–2.1 (68 H, H^b + PCy_3)				
10b	148–149 dec	51.0 (51.6)	8.6 (8.4)	4.4 (4.2)	1570, 1465, 1430, 500	C_6D_6	25	1.61 (2 H, dd, H^b), 2.57 (1 H, ttt, H^c), 3.57 (2 H, ddt, H^a)	1.36 (54 H)	6.9–7.3 (5 H, m, SPh)	−3.4 (s)[f]	
								J(H^a–H^b) = 1 Hz, J(H^a–H^c) = 8 Hz J(H^b–H^c) = 13 Hz, J(H^{a}–^{31}P) = 5 Hz, J(H^{c}–^{31}P) = 3 Hz				

11a	220–221 dec	55.5 (55.7)	8.4 (7.9)		1570, 1470, 1445, 510	toluene-d_8	25	2.80 (1 H, m, H^c), 3.63 (2 H, m, H^a)		6.8–7.6 (5 H, m, SePh)	50.7 (s)[f]	0.1
								0.80–2.2 (68 H, H^b + PCy_3)				
11b	151–152 dec	48.1 (48.7)	8.1 (7.9)		1570, 1465, 1430, 500	toluene-d_8	25	1.71 (1 H, d, 13 Hz, H^b), 2.50 (1 H, m, H^c), 3.73 (2 H, m, H^a)	1.38 (54 H)	6.3–7.3 (5 H, m, SePH)	0.7 (s)[f]	
12	144–145 dec	59.0 (59.4)	9.3 (8.9)		3050, 1490, 1210, 1070	toluene-d_8	25	2.38 (2 H, dd, H^e), 2.69 (2 H, dd, H^a), 2.95 (2 H, dd, H^b), 3.92 (2 H, dddd, H^c), 4.70 (2 H, ddd, H^d)	1.0–2.0 (33 H)		46.3 (s)[f]	
								$J(H^a–H^c)$ = 13 Hz, $J(H^b–H^c)$ = 10 Hz, $J(H^c–H^d)$ = 2 Hz, $J(H^c–H^e)$ = 11 Hz				
								$J(H^d–H^e)$ = 13 Hz, $J(H^a–^{31}P)$ = 4 Hz, $J(H^b–^{31}P)$ = 4 Hz, $J(H^d–^{31}P)$ = 6 Hz				
13	165.5–166.5 dec	60.9 (60.9)	9.6 (9.2)		3040, 1490, 1210, 1135, 1070, 990	C_6D_6	25	1.72 (6 H, d, CH_3[d]), 2.77 (2 H, dd, H^e), 2.80 (2 H, dd, H^e), 3.03 (2 H, dd, H^b), 4.00 (2 H, m, H^c)	1.0–2.0 (33 H)		46.7 (s)[f]	
								$J(H^a–H^c)$ = 14 Hz, $J(H^b–H^c)$ = 9 Hz, $J(H^c–H^e)$ = 9 Hz				
								$J(H^d–H^e)$ = 6 Hz, $J(H^a–^{31}P)$ = 4 Hz, $J(H^b–^{31}P)$ = 5 Hz				
14	151–152 dec	64.8 (65.2)	10.2 (9.8)		1640, 1440, 1140, 1000	C_6D_6	25	1.45 (3 H, d, 6 Hz, CH_3),[e] 4.02 (1 H, dd, 10 and 8 Hz, $=CH^b$), 4.53 (1 H, dd, 10 and 6 Hz, $=CH^a$), 8.97 (1 H, d, 8 Hz, CHO)	1.0–2.2 (66 H)[e]		38.0 (s)[f]	
15	175–176 dec	49.4 (49.7)	8.1 (7.5)	15.3 (15.7)	1445, 1380, 515	CD_2Cl_2	25	2.69 (1 H, d, H^b), 3.42 (1 H, dd, H^d), 3.63 (1 H, d, H^e), 4.53 (1 H, t, H^e),[g] 5.73 (1 H, dddd, H^c)	1.0–2.4 (33 H)		30.2 (s)[f]	0.7
								$J(H^a–H^c)$ = 7 Hz, $J(H^b–H^c)$ = 12 Hz, $J(H^c–H^d)$ = 14 Hz				
								$J(H^c–H^e)$ = 8 Hz, $J(H^d–^{31}P)$ = 9 Hz, $J(H^e–^{31}P)$ = 8 Hz				
16	144–146 dec	67.9 (67.5)	10.3 (9.7)	1.3 (1.8)	3300, 3050, 1600, 1510, 1450	toluene-d_8	25	3.40 (2 H, d, 4 Hz, CH_2NH), 4.6–4.8 (2 H, m, $=CH_2$), 5.3 (1 H, m, $=CH$), 6.4–7.2 (5 H, m, Ph)	0.8–2.2 (33 H)		43.8 (s)[f]	
17	128–129 dec	56.4 (57.0)	8.6 (8.5)		1570, 1450, 1420						25.1 (s)[f]	
24′	115–116 dec	56.3 (57.0)	8.3 (8.3)	1.3 (1.5)	3400, 2200	toluene-d_8	25	2.52 (1 H, br, H^c), 2.92 (2 H, br, H^a), 0.8–2.0 (68 H, H^b + PCy_3)[e]		1.58 (4 H, H_2O)[e]	41.7 (s)[f]	

[a] In KBr disks. [b] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Coupling patterns have been analyzed by homodecoupling, ^{31}P-decoupling, and triple-resonance techniques. Allylic signals are assigned by assuming that nuclei trans to PCy_3 (H^d and H^e in **3**, **8**, and **15**) couple with ^{31}P (ref 12a,b and references cited therein). [c] ppm from internal Me_4Si ($^{13}C\{^1H\}$ NMR) or external PPh_3 ($^{31}P\{^1H\}$ NMR) (downfield positive). Assignment of $^{13}C\{^1H\}$ NMR signals has been performed by off-resonance technique. Data with *f* are for $^{31}P\{^1H\}$ NMR, and the others are for $^{13}C\{^1H\}$ NMR. [d] EC = electric conductivity. Concentration of the compound is 0.5 mM. Measured at room temperature. Solvent is acetone for **3**, **4**, **7**, **8**, **9**, and **15** and THF for **10a** and **11a**. [e] Signals are overlapped with each other. [f] See footnote *c*. [g] There seem to be additional couplings among H^a, H^b, H^d, and H^e. [h] Complex **5** was characterized mainly by ^1H NMR. [i] Cooling a toluene solution of **6** to −78 °C gave a powder whose analytical data roughly agrees with a composition of $Pd(\eta^3\text{-}C_3H_5)(OPh)(PCy_3)$(toluene) (Calcd: C, 66.6; H, 8.3. Found: C, 67.6; H, 8.1): however, the powder seemed to contain PCy_3 or **7** and isolation of **6** was not feasible due to lack of suitable solvent for recrystallization.

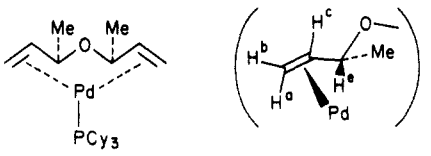
upon the substituent in the allyl group. A reaction of the simple allyl alcohol CH_2=$CHCH_2OH$ with **1** at 30 °C causes condensation of the allyl alcohol to yield diallyl ether and its coordination product, Pd(diallyl ether)(PCy_3) (**12**) (experiment 9). $^1H\{^{31}P\}$ NMR spectrum of **12** resembles that of its Ni analogue, Ni(diallyl ether)(PPh_3) (**18**),[11a] showing the same ABCDE spin pattern as observed for the allylic protons of **18**; the H^e(endo) signal appears at a considerably higher magnetic field than the H^d(exo) signal due to the diamagnetic shielding effect of Ni on H^e(endo).[11]



12

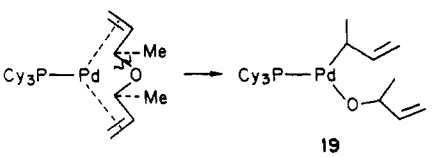
Complex **12** can be also prepared by the reaction of **1** with diallyl ether, and iodolysis of **12** and treatment of **12** with CO liberate diallyl ether quantiatively. Thermolysis of **12** at 150 °C in toluene in a sealed tube causes C–O bond cleavage to evolve propylene (14 mol %/**12**). In relation to the formation of **12** by the reaction of allyl alcohol with **1**, isolation of $PtCl_2$(diallyl ether) from a reaction mixture containing K_2PtCl_4 and allyl alcohol has been reported.[11b]

Use of 1-methylallyl alcohol (expt 10) similarly gave a mixture of *dl*-bis(1-methylallyl) ether, *meso*-bis(1-methylallyl) ether, and 1-methylallyl crotyl ether. However, among the ethers, only *meso*-bis(1-methylallyl) ether can coordinate to palladium probably by a steric reason and the isolated Pd complex was pure Pd(*meso*-bis(1-methylallyl)ether)(PCy_3) (**13**) as proven by elemental analysis and IR and NMR spectra. IR spectrum of **13** resembles that of **12** but has additional bands due to the CH_3 group (e.g., 1135 cm^{-1} assignable to $\nu(CCH_3)$). Comparison of ^1H NMR spectrum of **13** with that of **12** reveals that a signal assigned to H^d(exo) of **12** is lacking in the ^1H NMR spectrum of **13**; the ^1H NMR spectrum of **13** shows



13

a new peak at δ 1.72 assigned to CH_3 of **13**. The H^a, H^b, and H^c signals appear at almost the same positions as those observed for **12**, but the H^e signal appears at a somewhat lower magnetic field due to the change from the methylene proton to the methine proton by the CH_3 substitution. The CPK molecular model indicates that chelate coordination of the two C=C double bonds of *dl*-bis(1-methylallyl) ether is unlikely. The reaction of **13** with CO releases *meso*-bis(1-methylallyl) ether. Thermolysis of **13** at 170 °C in toluene in a sealed tube causes C–O bond cleavage to liberate 1-methylallyl alcohol (64%/**13**), 1,3-butadidne (trace), methyl vinyl ketone (36%/**13**), and 1-butene (trace). Liberation of these products suggests the occurrence of β-H shift in a supposed intermediate, Pd(1-methylallyl)[(1-methylallyl)oxo](PCy_3) (**19**). The β-H shift



13 **19**

from 1-methylallyl ligand to (1-methylallyl)oxo ligand in **19** affords 1-methylallyl alcohol and 1,3-butadiene, whereas the β-H shift from (1-methylallyl)oxo ligand to 1-methylallyl ligand gives methyl vinyl ketone and 1-butene. Most parts of 1,3-butadiene and 1-butene formed in the thermolysis seem to be oligomerized or polymerized during the thermolysis.

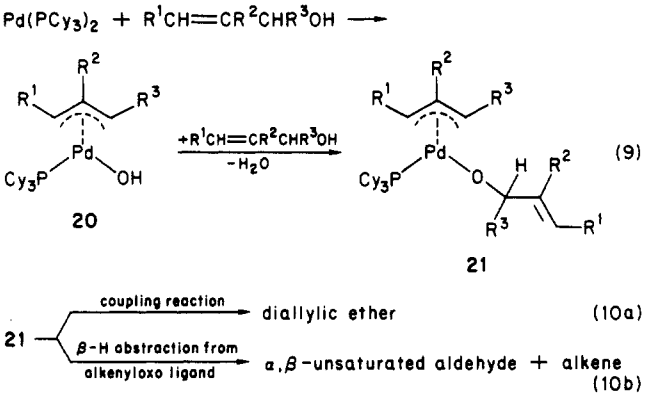
When crotyl alcohol is employed as the reactant (experiment 11), the reaction gives, besides the condensation products (a mixture of diallylic ethers), dismutation products of the reactant, namely, 1-butene and crotonaldehyde; the latter coordinates to Pd to form a π-complex, Pd(crotonaldehyde)(PCy_3)$_2$ (**14**). We previously reported

$$Pd(PCy_3)_2 + \text{crotyl alcohol} \rightarrow Pd(CH_3CH^a{=}CH^bCHO)(PCy_3)_2 + \text{crotonaldehyde} + \underset{14}{} \text{1-butene} + \text{condensation product} \quad (8)$$

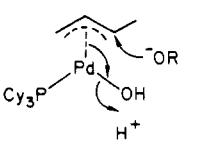
similar dismutation of allylic alcohols (allyl alcohol, crotyl alcohol, and 3-phenyl-2-propenyl alcohol) in the reactions of Ni(0) complexes.[11a]

Use of 2-methylallyl alcohol similarly gave methacrolein and *i*-butene, besides the condensation reaction product, di(2-methylallyl)ether and H_2O. In this case, however, both the ether and methacrolein can not coordinate to Pd, and black decomposition product of **1** is obtained.

These results of the reactions of allylic alcohols with **1** can be reasonably explained by assuming the formation of a common reaction intermediate, **21**, which is formed by the oxidative addition of allylic alcohol to Pd and the ensuing dehydration reaction between the oxidative addition product **20** and allylic alcohol. In relation to the



first step of reaction 9, formation of (η^3-allyl)palladium(II) complexes by reactions of allyl alcohol with palladium compounds has been reported.[16] Since diallylic ether is formed in every reaction (experiments 9–12), the coupling reaction (eq 10a) seems to be the more favorable pathway than the β-H abstraction from the alkenyloxo ligand in **21** (eq 10b). An alternative reaction route for the formation of ether involves external nucleophilic attack of allylic alcohol on the η^3-allylic ligand. At present we do not have



22

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Table III. Chemical Reactivities of Pd(η^3-C_3H_5)(OAc)(PCy_3) (3) and Pd(η^3-C_3H_5)(OC_6H_4CN)(PCy_3) (8) and Related Complexes

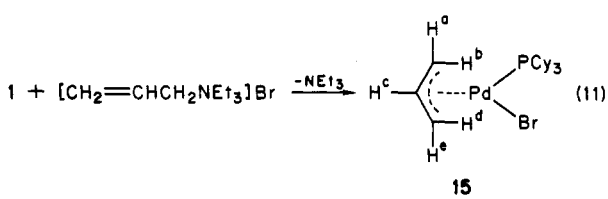
run	reactant (mol/complex)	complex	temp, °C	time	solv	product (% yield/complex): allylated compd[b]	product (% yield/complex): others
1	$NaCH(COOEt)_2$ (15)	3	rt[e]	2 h	THF	78	
2	$NaCH(COOEt)_2$ (1.0)	3	rt	2 h	THF	56	
3	$NaCH(COOEt)_2$ (34)	8	rt	1 h	THF	63	
4	$HNEt_2$ (ex)[a]	3	rt	5 h	none	41	
5	$HNEt_2$ (280) + allyl acetate (160)	1	17	6 h	none	7200	
6	$HNEt_2$ (97) + allyl acetate (190)	3	rt	4 h	none	1900	
7	$HNEt_2$ (190) + allyl acetate (380)	8	rt	4 h	none	3000	
8	$HNEt_2$ (ex)	8	rt	6 h	none	32	
9	$HNEt_2$(21) + allylamine (32)	8	rt	6 h	none		**24′** (30)
10	morpholine (ex)	3	18	2 days	none	49	
11	morpholine (ex)	6	rt	1 day	none	40	
12	morpholine (ex)	8	rt	1 h	none	36	
13	PCy_3 (1.3)	3	rt	1 h	acetone-d_6		**4** + **17**[c]
14	thermolysis	3	75	1 h	benzene		**17**[d]
15	CH_3I (ex)	3	rt	5 h	none		CH_3OAc (88)
16	CH_3I (ex)	8	rt	1 day	none		$CH_3OC_6H_4CN$ (46)
17	H_2SO_4 (ex)	3	rt	1 h	none		C_3H_6 (26)
18	H_2SO_4 (ex)	8	rt	1 h	none		C_3H_6 (22)
19	CO (ex)	3	rt	1 day	acetone		allyl acetate (55) + Pd–CO complex
20	CO (ex)	8	rt	1 day	toluene		$C_3H_5OC_6H_4CN$ (27) + Pd–CO complex

[a] ex = more than 40 mol/complex. [b] N- or C-monoallylated product of nucleophile. [c] Formation of considerable amounts of **4** and **17** was confirmed by $^{31}P\{^1H\}$ NMR. [d] Formation of a considerable amount of **17** was confirmed by an IR spectrum of the sample recovered after workup of the reaction mixture.

solid evidence to prove or disprove either mechanism. However, we favor the mechanism involving formation of **21**, since the dismutation reaction affording an aldehyde and an alkene suggests involvement of **21**. Preponderant evolution of 1-butene rather than 2-butenes in experiment 11 suggests that the hydride derived from the alkoxo ligand (eq 10b) preferentially attacks the allylic carbon with the alkyl substituent.

The reaction of **1** with a mixture of allyl alcohol and ethyl alcohol affords allyl ethyl ether besides diallyl ether (experiment 13) in support of a reaction mechanism involving formation of complex **20** which may further react with allyl alcohol and ethyl alcohol. No diethyl ether was detected in the reaction.

Allylamines. Addition of *N*-allyldiethylamine, CH_2=$CHCH_2NEt_2$, to **1** does not show any apparent change, whereas the reaction of $[CH_2$=$CHCH_2NEt_3]Br$ with **1** affords the oxidative addition product Pd(η^3-allyl)(Br)(PCy_3) (**15**). The ^1H NMR spectrum of **15** shows signals



(11)

15

characteristic of the η^3-allyl ligand. Two reaction mechanisms are conceivable for the formation of **15**. One is the mechanism involving oxidative addition of allyl bromide partly formed from $[CH_2$=$CHCH_2NEt_3]Br$, and another mechanism involves oxidative addition of $[CH_2$=$CHCH_2NEt_3]^+$ to Pd to give $[Pd(\eta^3\text{-}C_3H_5)(PCy_3)(NEt_3)]Br$ (**23**) and its subsequent rearrangement to afford **15** and NEt_3.

The reaction of *N*-allylaniline with **1** gives Pd(*N*-allylaniline)(PCy_3) (**16**), and no oxidative addition product is isolated even after the reaction at 70 °C. The IR spectrum of **16** is consistent with the formulation, showing peaks due to *N*-allylaniline and PCy_3. The ^1H NMR spectrum of **16** shows only a small shift (ca. 0.3 ppm) of signals of olefinic protons of *N*-allylaniline on adduct formation. The NH signal was not detected presumably due to overlapping with other peaks or due to its too broad shape. The small shift of the olefinic signals suggests the possibility that *N*-allylaniline serves as a solvent of recrystallization and does not interact with Pd. However, after repeated recrystallization of **16** from hexane containing no added *N*-allylaniline, **16** can be recovered; consequently we believe that *N*-allylaniline in **16** has a fairly strong interaction with Pd. No apparent change was observed on treatment of **1** with *N*-allylphthalimide and *N*-allylthiourea, and the starting complex **1** was recovered.

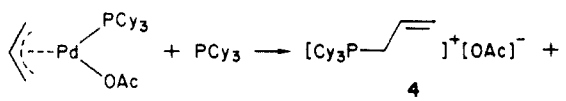
Other Related Reactions. It is known that interaction of aryl and vinyl carboxylates with Ni(0) complexes causes oxidative addition of the ester to Ni through the C–O bond cleavage.[17] However, treatment of **1** with these esters showed no apparent change even at elevated temperatures (70–100 °C). Allyl cyanide did not react with **1** either. The reaction of allyl ethyl carbonate (3 mol/1) with **1** (room temperature, 6 h) causes the decarboxylation reaction to afford allyl ethyl ether (27 mol %/1), CO_2 (67 mol %/1), and ethyl alcohol (59 mol %/1). Use of allyl phenyl carbonate under similar conditions gives similar products (allyl phenyl ether, CO_2, and phenol).

Properties of Isolated Pd Complexes and Their Chemical Reactivities Related to Catalysis. The Pd(η^3-C_3H_5)(X)(PCy_3)-type complexes (**3**, **8**, and **15**) show only a small electric conductivity in acetone compared with those of phosphonium salts **4**, **7**, and **9** (last column of Table II), revealing that the complexes are essentially nonionic. Addition of a base, NEt_3, in excess (19 mol/8) to the acetone solution of **8** does not change the electric

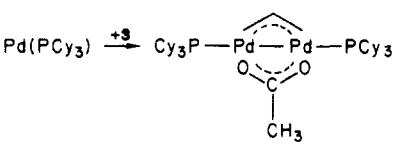
(17) Yamamoto, T.; Ishizu, J.; Kohara, T.; Komiya, S.; Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 3758–3764.

conductivity, indicating that replacement of the OC_6H_4CN ligand by NEt_3 to give an ionic species (e.g., $[Pd(\eta^3\text{-}C_3H_5)(PCy_3)(NEt_3)]^+[OC_6H_4CN]^-$) is not an easy process. Complexes **3**, **8**, and **15** and the dinuclear complexes **10** and **11** are rather insensitive to air in the solid, but their solutions tend to degrade in air.

Table III summarizes the products of the reactions of **3** and **8** with various reagents. Complexes **3** and **8** react with nucleophiles including $HNEt_2$, morpholine, and $NaCH(COOEt)_2$ to afford the corresponding allylated products (runs 1–12 in Table III). Attack of the nucleophile on the η^3-allyl ligand explains the results. Complex **3** reacts with PCy_3 to yield the propenylphosphonium salt **4** and the dinuclear complex **17**, which is considered to be formed by a reaction of **3** and $Pd(PCy_3)$ generated from **3** after the reaction of PCy_3 with **3**. The NMR spectrum



3 **4**

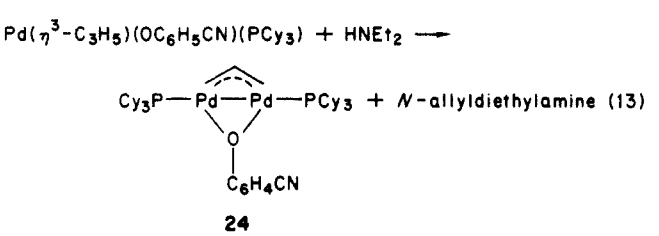


(12)

17

of **17** does not show clear allylic signals, and **17** has been characterized by elemental analysis, chemical reactivities, and comparison of its IR spectrum with that of a sample prepared by the reaction of $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}OAc)]_2$ with $Pd(PCy_3)_2$ according to Werner's method.[15a]

Because of the occurrence of the reaction expressed by eq 12, the preparation of **3** and **4** by the reaction of **1** with allyl acetate sometimes accompanies the formation of **17**, especially when the initial concentration of **1** is high or not enough allyl acetate is added. The formation of the binuclear type complex is not restricted to the case of allyl acetate, but most of the allylation of nucleophiles by $Pd(\eta^3\text{-allyl})(OY)(PCy_3)$ seems to be accompanied by the formation of similar binuclear complexes. Actually a complex, which is assignable to $Pd_2(\mu\text{-}C_3H_5)(\mu\text{-}OC_6H_4CN)(PCy_3)_2$ (**24**)[18] on the basis of elemental analysis and ^1H NMR, is isolated from the reaction mixture containing **8** and $HNEt_2$. The results indicate that $Pd(PCy_3)$



24

generated from **1** after the allylation of $HNEt_2$ is trapped by **8** to form **24**. The dinuclear complexes **17** and **24** are inert against nucleophiles.

As described above, $Pd(PCy_3)$ generated from **3** and **8** after the allylation of nucleophiles is trapped by **3** and **8** to form the dinuclear complexes having negligible reactivity against nucleophiles. However, when excess amounts of allylic compounds like allyl acetate are present in the reaction system, $Pd(PCy_3)$ is not inactivated as the binuclear complexes are. Under the circumstances $Pd(PCy_3)$ reacts with the allylic compound to regenerate **3** or **8**. Thus, **1**, **3**, and **8** (runs 5–7) serve as catalysts for the allylation of $HNEt_2$ by allyl acetate.

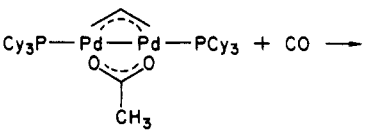
Treatment of **3** and **8** with carbon monoxide gives allyl acetate and *p*-cyanophenyl ether, respectively, indicating that the oxidative addition process of allyl acetate and allyl *p*-cyanophenyl ether to Pd is reversible.

$$Pd(\eta^3\text{-}C_3H_5)(OY)(PCy_3) + CO \rightarrow C_3H_5OY + Pd(CO)_m(PCy_3)_n \quad (14)$$

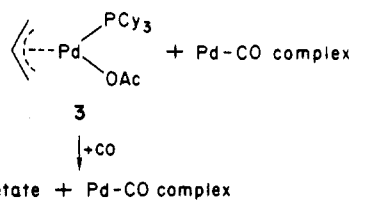
$$Y = OAc,\ OC_6H_4CN$$

Reactions of **3** and **8** with CH_3I give methyl acetate and methyl *p*-cyanophenyl ether, respectively, but the methylation product of the η^3-allyl ligand (1-butene) was not detected in the reaction product. The acidolysis of **3** and **8** by concentrated H_2SO_4 liberates propylene.

The dinuclear complexes **10**, **11**, **17**, and **24** are inert against nucleophiles as described above. The acidolysis of **10** with concentrated H_2SO_4 liberates propane. The reaction of **17** with CO initially gives **3**, which further reacts with CO to afford allyl acetate and Pd–CO complexes, indicating the occurrence of the following series of reactions.



17



3

Experimental Section

Materials, Manipulation of Complexes, Analysis, and Instrumentation. $Pd(PCy_3)_2$,[8] $Pd(P\text{-}t\text{-}Bu_3)_2$,[8] $Pd(PPh_3)_4$,[7] $Pd(CH_2{=}CH_2)(PPh_3)_2$,[8a] and $[Pd(\eta^3\text{-}C_3H_5)(OAc)]_2$[19] were prepared according to the literature. Allyl phenyl sulfide was donated from Professor Takei of our institute. The $PCy_3{\cdot}CS_2$ adduct was donated from Mr. Kitazume of Mitsubishi Petrochemical Co. Ltd., and PCy_3 was generated from the adduct by removing CS_2 by heating the adduct in ethyl alcohol and was recrystallized from ethyl alcohol. Allyl *p*-cyanophenyl ether was synthesized by Williamson's method.[20] 2-Methylallyl acetate was synthesized by the reaction of 2-methylallyl alcohol (64.9 g, 0.90 mol) with acetic acid (91.9 g, 0.90 mol) in the presence of pyridine (71.1 g, 0.90 mol) at room temperature. Allyl phenyl selenide was synthesized according to the literature.[21] Purities of these reactants were confirmed by ^1H NMR. $CH_2{=}CHCD_2OAc$ was prepared via (i) reduction of $CH_2{=}CHCOCl$ with $LiAlD_4$ in ether and (ii) reaction between $CH_2{=}CHCD_2OH$ and acetic anhydride in the presence of pyridine.[22] ^1H NMR: δ 2.04 (3 H, s, CH_3), 5.09–5.20 (2 H, m, $=CH_2$), 5.71–6.25 (1 H, m, $=CH$). $CH_2{=}CHCD_2OAc$ thus prepared contained diethyl ether (about 15 vol % estimated from ^1H NMR). An attempt to isolate $CH_2{=}CHCD_2OAc$ by GLC using a poly(ethylene glycol) column was not successful due to the occurrence of the 1,3-shift in the column. Other reactants listed in Tables I and III and in the text were purchased from

(18) Complex **24** was obtained as its hydrated product $Pd_2(\mu\text{-}C_3H_5)(\mu\text{-}OC_6H_4CN)(PCy_3)_2{\cdot}2H_2O$ (**24'**) by absorption of moisture during the workup process (see Experimental Section).

(19) Robinson, S. D.; Shaw, B. L. *J. Organomet. Chem.* **1965**, *3*, 367–370.
(20) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 4th Ed.; Allyn and Bacon: Boston, 1983; p 537.
(21) Kataev, E. G.; Kataev, L. M.; Chmutova, G. A. *Zh. Org. Chim.* **1966**, *2*, 2244–2248.
(22) Schuetz, R. D.; Millard, F. W. *J. Org. Chem.* **1959**, *24*, 297–300.

Tokyo Kasei Co. Ltd. or Wako Co. Ltd. and purified by distillation. Dicrotyl ether and 1-methylallyl crotyl ether as the authentic samples for GLC analysis of the products in experiments 10 and 11 were prepared by Williamson's method.[20] Solvents were dried over Na, CaH_2, P_2O_5, or drierite ($CaSO_4$), distilled under N_2 or Ar, and stored under N_2 or Ar. Reactions were generally carried out in Schlenk tubes under an atmosphere of N_2 or Ar under vacuum. Manipulation of complexes was performed under N_2 or Ar. Melting points were measured in sealed glass capillaries under vacuum. GLC analysis was performed with Shimadzu GC-3B, GC-6A, and GC-3BF instruments (carrier gas is He for GC-3B and GC-6A and N_2 for GC-3BF). SSE-30, SDC-550, Porapak Q, and VZ-7 purchased from Gaschro-Kogyo Co. Ltd. were used to prepared the columns. Amounts of gases evolved in reactions were measured by a Topler pump and analyzed by GLC. GC–mass spectra were recorded on a Hitachi M-80 GC–mass spectrometer (column is OV-1 or SE-30: carrier gas is He). Electric conductivity of the solutions of complexes was measured with a TOA Denpa CM-5B electrometer. IR spectra were recorded on a Hitachi Model 295 spectrometer by using KBr disks under N_2. ^1H NMR spectra were recorded on a Japan Electron Optics Laboratory (JEOL) Model JNM-PS0100, FX-100, or FX-400 spectrometer and ^{13}C and ^{31}P NMR spectra on a JEOL Model JNM-PET-PS-100 Fourier transform spectrometer.

Reactions of Allylic Compounds with PdL_2 (Cf. Table I). Experiment 1. A homogeneous mixture of **1** (620 mg, 0.93 mmol) and allyl acetate (8.9 g, 89 mmol) was stirred at room temperature. After 10 min, a white powder of **4** started to precipitate. After 12 h, the white precipitate and yellowish solution were separated by filtration. Recrystallization from acetone gave **4**: yield, 43%; mp 107–109 °C. Anal. Calcd for ($C_{23}H_{41}O_2P$): C, 72.6. Found: C, 71.8. The disagreement between the found and calculated values seems to be due to partial incorporation of H_2O into **4** due to its hygroscopic nature.

The volatile materials in the yellowish filtrate obtained after removal of **4** were removed by evaporation in acetone (ca. 30 mL) and kept in a dry ice box to yield slightly colored (yellow) crystals of **3**: yield, 43%; mp 134–136 °C dec. Anal. ($C_{23}H_{41}O_2PPd$) C, H. Compound **3** was prepared also by the following pathways. An ethereal solution (3 mL) of PCy_3 (290 mg, 1.03 mmol) was added dropwise to $[Pd(\eta^3\text{-}C_3H_5)(OAc)]_2$ (220 mg, 0.53 mmol) dispersed in 15 mL of diethyl ether at −78 °C with stirring. Stirring the mixture for 10 min at −78 °C gave a homogeneous yellow solution. Then, the reaction temperature was raised to room temperature. After the reaction mixture was stirred for 30 min at room temperature, ether was removed by evaporation to obtain a yellow solid of **3**, which was recrystallized from acetone and found to be identical with that obtained in experiment 1 by IR and ^1H NMR spectroscopy; yield, 73%. The reaction of **1** (550 mg, 0.83 mmol) with $CH_2{=}CHCD_2OAc$ (1.5 mL) was carried out similarly to experiment 1 (room temperature, 5 h).

Experiments 2–15. Other reactions of **1** and **2** with the allylic compounds were carried out analogously under conditions listed in Table I.

Preparation of $Pd_2(\mu\text{-}C_3H_5)(\mu\text{-}OAc)(PCy_3)_2$ (17). $[Pd(\eta^3\text{-}C_3H_5)(OAc)]_2$ (77 mg, 0.19 mmol) was dissolved in 5 mL of diethyl ether. After the solution was cooled to −78 °C, $Pd(PCy_3)_2$ (240 mg, 0.37 mmol) was added. The reaction mixture was stirred at −20 °C to yield a white precipitate. The precipitate was recrystallized from ether–toluene; yield, 89%. Complex **17** was prepared also by the reaction of **1** (1.2 g, 1.7 mmol) and allyl acetate (8.0 g) at room temperature (2 h). The yellow precipitate was separated by filtration. Extraction of the yellow solid with toluene and evaporation of the toluene extract gave a yellow solid (yield of **17**, 29%), which was recrystallized from toluene–hexane.

Preparation of $Pd_2(\mu\text{-}C_3H_5)(\mu\text{-}OC_6H_4CN)(PCy_3)_2{\cdot}2H_2O$ (24'). A mixture of **8** (110 mg, 0.21 mmol), diethylamine (0.34 g, 4.6 mmol), and *N*-allyldiethylamine (760 mg, 6.7 mmol) was stirred for 6 h at room temperature. After volatile materials were removed in the reaction mixture, the residue was dissolved in acetone (5 mL). The acetone solution was kept in a dry ice box to give yellow transparent crystals, which were separated by filtration, washed with acetone at −78 °C, and dried under vacuum to yield **24'**: yield, 59%; mp 115–116 °C dec.

Reactions of (η^3-Allyl)palladium and Related Complexes (Cf. Table III). Run 1. A THF (5-mL) solution of $NaCH(COOEt)_2$ was prepared by a reaction of $CH_2(COOEt)_2$ (390 mg, 2.4 mmol) and NaH (53 mg, 2.2 mmol). Complex **3** (66 mg, 0.14 mmol) and diphenyl ether (internal standard for GLC) were added to the solution, and the reaction mixture was stirred for 2 h at room temperature. GLC analysis showed formation of 0.11 mmol of $CH_2{=}CHCH_2CH(COEt)_2$.

Other reactions listed in Table III were carried out under conditions analogous to those shown in Table III.

Reaction of 3 with PCy_3. Complex **3** (41 mg, 0.085 mmol) and PCy_3 (32 mg, 0.11 mmol) were put in an NMR tube, into which acetone-d_6 was added. $^{31}P\{^1H\}$ NMR spectrum taken after the sample was allowed to stand for 1 h at room temperature showed peaks of **3**, **4**, and **17** (relative peak height = 1:2.6:0.7). An uncharacterized peak at 60.6 ppm was also observed.

Reaction of 17 with CO. Complex **17** was placed in an NMR tube, where CD_2Cl_2 was added. The atmosphere in the NMR tube was replaced by CO (1 atm). After 1 h at room temperature the ^1H NMR spectrum showed allylic peaks characteristic of **3**, and after 2 h the ^1H NMR spectrum showed formation of **3** and allyl acetate (ca. 1:1). After 24 h the peaks of **3** almost disappeared and the ^1H NMR spectrum showed formation of allyl acetate (ca. 50%/**17**).

Thermolysis of 13. A toluene solution (1 mL) containing 48 mg (0.093 mmol) of **13** was heated for 5 h at 170 °C (temperature of the oil bath) in a sealed tube. GLC analysis showed formation of butadiene, butenes, 1-methylallyl alcohol, and methyl vinyl ketone (see text).

Registry No. **1**, 33309-88-5; **2**, 53199-31-8; **3**, 79270-04-5; **4**, 79251-35-7; **5**, 79270-05-6; **6**, 89370-98-9; **7**, 102588-88-5; **8**, 89370-92-3; **9**, 102588-89-6; **10a**, 89370-93-4; **10b**, 89370-95-6; **11a**, 89370-94-5; **11b**, 89370-96-7; **12**, 89370-97-8; **13**, 102588-83-0; **14**, 102588-84-1; **15**, 102588-85-2; **16**, 102588-86-3; **17**, 102588-87-4; $Pd_2(\mu\text{-}C_3H_5)(\mu\text{-}OC_6H_4CN)(PCy_3)_2$, 102615-67-8; $[Pd(\eta^3\text{-}C_3H_5)(OAc)]_2$, 12084-71-8; *trans*-$C_4H_8$, 624-64-6; *cis*-$C_4H_8$, 590-18-1; 1-$C_4H_8$, 106-98-9; Pd, 7440-05-3; $CH_2{=}CHCH_2OCOCH_3$, 591-87-7; $CH_2{=}C(CH_3)CH_2OCOCH_3$, 820-71-3; $CH_2{=}CHCH_2OC_6H_5$, 1746-13-0; $CH_2{=}CHCH_2OC_6H_4$-*p*-CN, 33148-47-9; $CH_2{=}CHCH_2SC_6H_5$, 5296-64-0; $CH_2{=}CHCH_2SeC_6H_5$, 14370-82-2; $CH_2{=}CHCH_2OH$, 107-18-6; $CH_2{=}CHCH(CH_3)OH$, 598-32-3; $CH_3CH{=}CHCH_2OH$, 6117-91-5; $CH_2{=}C(CH_3)CH_2OH$, 513-42-8; $[CH_2{=}CHCH_2NEt_3]Br$, 29443-23-0; $CH_2{=}CHCH_2NHC_6H_5$, 589-09-3; diallyl ether, 557-40-4; *meso*-bis(1-methylallyl) ether, 10291-16-4; *dl*-bis(1-methylallyl) ether, 6925-74-2; 1-methylallyl crotyl ether, 1476-05-7; butadiene, 106-99-0; dicrotyl ether, 1476-04-6; methacrolein, 78-85-3; isobutene, 115-11-7; diallyl ether, 557-40-4; allyldiethylamine, 5666-17-1.