Reactions of π-Allylic Palladium(II) Complexes of Acetoacetate Esters with Pyridine and Its Derivatives

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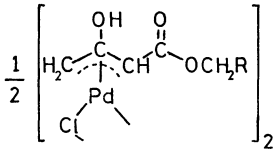
The π-allylic palladium(II) complexes of ethyl and benzyl acetoacetate esters react with pyridine and its derivatives to afford the terminal-carbon-bonded complexes $PdCl(CH_2COCH_2COOCH_2R)L_2$, where R=$CH_3$ or C_6H_5, and L=pyridine or its derivative. The NMR spectra unequivocally establish the bonding type in these complexes. The pyridine and 4-methylpyridine complexes are a mixture of *cis* and *trans* isomers in a ratio of 1:5, while 2-methyl- and 2,6-dimethyl-pyridine complexes are *trans* exclusively. The relative stabilities of these complexes are compared.

In a previous paper[1] we reported on the central-carbon-bonded palladium(II) complexes of acetylacetone obtained by the reactions of bis(acetylacetonato)-palladium(II) with triphenylphosphine or nitrogen bases such as pyridine, diethylamine and *N*-methylbenzylamine. This paper describes the preparation and characterization of the terminal-carbon-bonded palladium(II) complexes of acetoacetate esters.[2]

Results and Discussion

The π-allylic palladium(II) complex of ethyl acetoacetate, di-μ-chlorobis(π-1-ethoxycarbonyl-2-hydroxyallyl)dipalladium(II) [**1**] was prepared by the reaction of diketene with the tetrachloropalladate(II) in ethanol.[3] The corresponding complex of benzyl acetoacetate [**2**] was obtained by the reaction of diketene with dichlorobis(benzonitrile)palladium(II)in dichloromethane containing benzyl alcohol.

π-Allylic palladium(II) complexes of acetoacetate esters reacted with excess pyridine or its derivatives in benzene at room temperature to yield stable terminal-carbon-bonded complexes in high yields (82—95%).

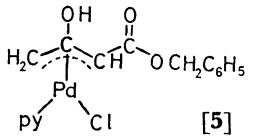


R=CH_3 [**1**] or C_6H_5 [**2**]

⟶ $PdCl(CH_2COCH_2COOCH_2R)L_2$ (i)

R=CH_3, L=py [**3a**] or 1/2(2,2′-bipy) [**3b**]
R=C_6H_5, L=py [**4a**], 2-Me-py [**4b**], 4-Me-py [**4c**], 2,6-Me_2-py [**4d**], or 1/2(2,2′-bipy) [**4e**]

Analytical data of the products are summarized in Table 1. The conversion of the π-allylic linkage of the acetoacetate ligand into the σ-bonding seems to be preceded by the bridge splitting reaction of the dimeric complex. A monomeric π-allylic complex [**5**] was isolated as yellow-green crystals in the reaction of the



[**5**]

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TABLE 1. TERMINAL-CARBON-BONDED PALLADIUM(II) COMPLEXES OF ACETOACETATE ESTERS

Complex[a]	Color	Anal, found (calcd) % C	H	N	Mol wt[b] found (calcd)	Dec. temp °C
PdClY-$(py)_2$	pale yellow	44.47 (44.75)	4.44 (4.44)	6.55 (6.53)	430 (429)	110
PdClY-(bipy)	yellow	44.42 (44.99)	3.92 (4.01)	6.75 (6.56)	410 (427)	166
PdClY′-$(py)_2$	pale yellow	50.79 (51.34)	4.36 (4.30)	6.01 (5.70)	480 (491)	107
PdClY′-(2-Me-py)$_2$	yellow	52.82 (53.19)	4.89 (4.85)	5.65 (5.40)	512 (519)	104
PdClY′-(4-Me-py)$_2$	pale yellow	52.61 (53.19)	4.98 (4.85)	5.65 (5.40)	500 (519)	105
PdClY′(2,6-Me_2-py)$_2$	yellow	53.86 (53.97)	5.31 (5.43)	5.36 (5.03)	540 (556)	136
PdClY′-(bipy)	yellow	51.44 (51.55)	4.02 (3.91)	5.82 (5.73)	483 (489)	145

a) Y=$CH_2COCH_2COOCH_2CH_3$, Y′=CH_2COCH_2-$COOCH_2C_6H_5$. b) Determined in dichloromethane at 25 °C.

benzyl ester complex with an equivalent amount of pyridine.

IR Spectra. The IR spectra of the parent π-allylic complexes **1** and **2** have the ν(OH) and ν(C=O) bands at around 3200 and 1670 cm^{-1}, respectively. On the other hand, the product complexes **3** and **4** show no absorption band around 3200 cm^{-1}, but exhibit two strong ν(C=O) vibrations at around 1730 and 1640 cm^{-1} (Table 2). This demonstrates that the π-allylic linkage of the enolate anion of acetoacetate esters was converted into the σ-carbon-bonding of the ketonic tautomer.

Two modes of linkage can be considered for the unidentate carbon-bonding of the acetoacetate ester to palladium(II), terminal-carbon-bonding (**A**) and central-carbon-bonding (**B**).

Pd–$CH_2COCH_2COOCH_2R$ (**A**)

$CH_3COCHCOOCH_2R$ (**B**)

Structure **B** was realized in the case of acetylacetone, and the ν(C=O) vibrations of the central-carbon-bonded ligand causes absorption at 1665 and 1632 cm^{-1}.[1] If this were also the case for the acetoacetate-ester ligand, the ν(C=O) bands should appear in the 1600—

Table 2. Characteristic IR bands (cm^{-1}) in Nujol[a]

Complex[b]	ν(OH)	ν(C=O) ketone	ν(C=O) ester	ν(Pd–C)	ν(Pd–Cl)	ν(Pd–N)
Starting complex[1]	3200m		1675vs	548s[c]	270s	
PdClY $(py)_2$ [3a]		1650vs	1740vs	540s	283s, 355m	250m
PdClY (bipy) [3b]		1640vs	1730vs	543s	335s	243m
Starting complex[2]	3220m		1670vs	498s[c]	265m	
PdClY′ $(py)_2$ [4a]		1645vs	1735vs	508s	321s, 357w	240m
PdClY′(2-Me-py)[4b]		1640s	1730vs	498s	288s	250m
PdClY′(4-Me-py)$_2$[4c]		1655vs	1740vs	507s	260s	255sh
PdClY′(2,6-Me_2-py)$_2$ [4d]		1660vs	1745vs	498s	305s	258s
PdClY′ (bipy) [4e]		1635vs	1730vs	504s	328s	240m
π-Allylic monomer[5]	3200w		1675vs			

a) vs: very strong, s: strong, m: medium, w: weak, sh: shoulder. b) Y=$CH_2COCH_2COOCH_2CH_3$, Y′=CH_2-$COCH_2COOCH_2C_6H_5$ c) π-allylic skeletal deformation

1700 cm^{-1} region. Contrary to expectation, the IR spectra of compounds **3** and **4** showed a ν(C=O) band in the 1600—1700 cm^{-1} region and another one in the frequency region higher than 1700 cm^{-1}. The spectra can be interpreted satisfactorily on the basis of structure **A**.

The ν(C=O) vibrations of the keto tautomer of free acetylacetone cause absorption at 1727 and 1707 cm^{-1},[4] but shift towards the lower frequency region (1665 and 1632 cm^{-1}) by ligation to the palladium atom *via* the central carbon atom.[1] When the acetoacetate-ester ligand coordinates to the palladium atom *via* the terminal carbon atom, the ν(C=O) band due to the ketonic carbonyl group should shift towards the lower frequency side to an extent similar to that in the case of central-carbon ligation. On the other hand, the ester carbonyl group is situated far from the metal atom and is far less influenced by coordination. Thus, of the two observed ν(C=O) bands of compounds **3** and **4**, the lower frequency band is assigned to the ketonic carbonyl group and the higher frequency one to the ester carbonyl group.

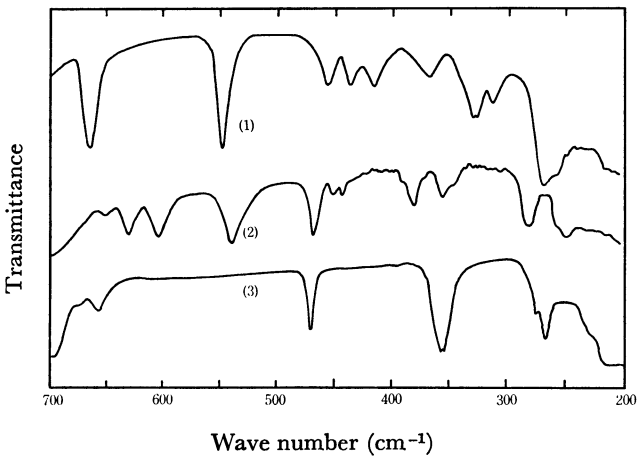


Fig. 1. The IR spectra in the 700—200 cm^{-1} region of the π-allylic palladium(II) complex dimer of ethyl acetoacetate (curve 1), PdCl($CH_2COCH_2COOC_2H_5$)-$(py)_2$ (curve 2) and *trans*-$PdCl_2(py)_2$ (curve 3) in Nujol mull.

For the sake of comparison the IR spectrum of the carbon-bonded bis(pyridine) complex **3a** in the 700—200 cm^{-1} region is shown together with spectra of the parent π-allylic complex **1** and *trans*-$PdCl_2(py)_2$ in Fig. 1. The spectrum of complex **1** is readily interpreted by reference to the metal isotope effect reported by Shobatake and Nakamoto[5] on the metal-ligand vibrations in π-allyl complexes of palladium(II). Thus the strong band at 548 cm^{-1} (curve 1) corresponds to the 512 cm^{-1} peak in $[PdCl(C_3H_5)]_2$ and is assigned to the CCC bending mode. The three-peaks pattern in the 460—410 cm^{-1} region resembles that of the latter compound in the 410—350 cm^{-1} region, and is ascribed to ν(Pd-allyl) vibrations. The strongest peak at 270 cm^{-1} accompanied by a shoulder at 255 cm^{-1} is similarly attributed to the bridging Pd–Cl stretching vibrations. These assignments are also consistent with those of Adams and Squire[6] for $[PdCl(C_3H_5)]_2$. Neither a strong peak at 665 cm^{-1} nor bands in the 370—310 cm^{-1} region are observed for $[PdCl(C_3H_5)]_2$. These are considered to be due to the ligand vibrations.

The spectrum of *trans*-$PdCl_2(py)_2$ is very simple (curve 3, Fig. 1). The bands observed at 357 and 268 cm^{-1} are assigned to the ν(Pd–Cl) and ν(Pd–N) vibrations, respectively. Pfeffer *et al.*[7] observed the ν(Pd–Cl) bands at 358, 356, and 373 cm^{-1}, and the ν(Pd–N) bands at 278, 302, and 306 cm^{-1} for *trans*-$PdCl_2L_2$ with pyridine, 4-methylpyridine and 4-ethylpyridine as L, respectively. Norbury and Sinha also observed the ν(Pd–Cl) bands at 360 and 359 cm^{-1} for *trans*-$PdCl_2(AsPh_3)_2$ and *trans*-$PdCl_2(PPh_3)_2$, respectively.[8]

The spectrum of PdCl($CH_2COCH_2COOC_2H_5$)$(py)_2$ [**3**] (curve 2, Fig. 1) is much more complicated than that for *trans*-$PdCl_2(py)_2$ (curve 3). As is revealed by the NMR spectra, the compound is a mixture of *cis* and *trans* isomers in a ratio *ca.* 1:5. The strong band at 283 cm^{-1} is assigned to the stretching vibration of the Pd–Cl bond *trans* to the alkyl ligand, since the possibility of chloride bridging is excluded by analytical and molecular-weight data (Table 1). The strong *trans*-influence of the alkyl ligand is well-known[9]. Another band (355 cm^{-1}) and a shoulder (347 cm^{-1}) in the terminal ν(Pd–Cl) region might be ascribed to the ν(Pd–Cl) vibration in the *cis* isomer. The broad band of medium intensity at 250 cm^{-1} is assigned to the ν(Pd–N) vibration. The frequency is a little lower than 268 cm^{-1} in *trans*-$PdCl_2(py)_2$.

Three bands are observed in the 640—500 region where *trans*-$PdCl_2(py)_2$ has no absorption. The strong peak at 540 cm^{-1} is assigned to the ν(Pd–C) vibration. In recent years an increasing number of palladium(II) complexes containing the Pd–C linkage have been reported, but data of the ν(Pd–C) vibration are rather

Table 3. NMR data for methylene protons in the terminal-carbon-bonded palladium(II) complexes of acetoacetate esters[a)]

Complex[b)]	CH_2[(a)]		CH_2[(b)]		CH_2[(c)]	
$PdClY(py)_2$ [**3a**]	7.33	7.16	7.03	6.16	5.87[c)]	5.80[c)]
PdClY(bipy) [**3b**]		7.13		6.00		5.86[c)]
$PdClY'(py)_2$ [**4a**]	7.27	7.03	6.90	6.03	4.80	4.76
$PdClY'(2\text{-Me-py})_2$ [**4b**]	7.48		6.93		4.93	4.88
$PdClY'(4\text{-Me-py})_2$ [**4c**]	7.37	7.20	6.90	6.10	4.83	4.80
$PdClY'(2,6\text{-Me}_2\text{-py})_2$ [**4d**]	7.70		7.33		5.00	
PdClY'(bipy) [**4e**]		7.13		5.96		4.83

a) Chemical shift (τ) recorded at 60 MHz in $CDCl_3$ with Me_4Si as the internal reference. Signals are singlet unless otherwise stated. b) $Y=CH_2^{(a)}COCH_2^{(b)}COOCH_2^{(c)}CH_3$, $Y'=CH_2^{(a)}COCH_2^{(b)}COOCH_2^{(c)}C_6H_5$. c) Quartet, $J=7$ Hz.

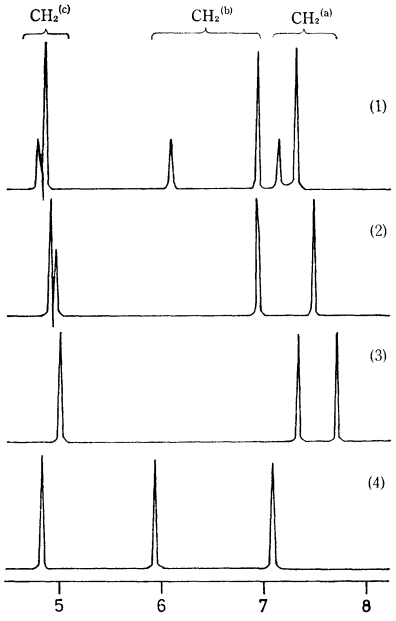


Fig. 2. The NMR spectra of $PdCl(CH_2^{(a)}COCH_2^{(b)}COOCH_2^{(c)}C_6H_5)L_2$ in the methylene signal region recorded at 60 MHz with TMS as an internal reference in $CDCl_3$: L=py (curve 1), 2-Me-py (curve 2), 2,6-Me_2-py (curve 3), or 1/2 (2,2'-bipy) (curve 4).

scarce. The ν(Pd–C) bands in the Pd(2,4-pentanedionato-O,O')(2,4-pentanedionato-C^3)L complexes were observed at 540, 524, 519, and 518 cm^{-1} for L= PPh_3, py, $NHEt_2$, and $NH(Me)CH_2Ph$, respectively.[1)] Dietl *et al.* reported that the peak at 487 or 530 cm^{-1} is assigned to the ν(Pd–C) vibration in $[PdCl_2(C_2Me_2)_3]_2$.[10)] Other bands appearing in the 700—600 and 500—370 cm^{-1} regions seem to be due to ligand vibrations (curve 2, Fig. 1).

Characteristic IR bands of each of the terminal-carbon-bonded palladium(II) complexes of acetoacetate esters were assigned in a similar way and are given in Table 2.

NMR Spectra. The NMR spectra of products **3** and **4**, summarized in Table 3, unequivocally establish structure **A**. A spectrum of the benzyl ester complex **4e** involving 2,2'-bipyridine as a base exhibits three singlet peaks of equal intensity at 7.13, 5.96, and 4.83 τ (Fig. 2). These are assigned to the three methylene groups; the nearest to palladium, the central and the benzyl methylenes, respectively.

Geometrical isomerism is possible in the case of complexes containing unidentate ligands, both *cis* and *trans* isomers being formed, but not in the case of 2,2'-bipyridine complexes. The spectrum of the pyridine complex **4a** involves two sets of methylene signals. Chemical shifts of the three minor peaks are close to those of the methylene signals of the 2,2'-bipyridine complex **4e**, suggesting that they are attributable to the *cis* isomer of **4a**. The other set of stronger peaks are thus assigned to the *trans* isomer. The intensity ratio of the *trans* and *cis* peaks is nearly equal for each of the three methylene signal pairs amounting to *ca.* 5:1. Isomerization of palladium(II) complexes is usually slow in the absence of free ligands,[11)] and the observed figure reflects the relative yield of the two isomers in reaction (i). A single crystal of compound **4a** submitted for X-ray analysis was composed of *cis* molecules.[12)]

The same situation was also observed for the 4-methylpyridine complex **4c**. Only three methylene signals, however, were observed for the 2,6-dimethylpyridine complex **4d**. Their chemical shifts are higher than those for the *trans* isomer of the pyridine complex **4a**. Thus it seems reasonable to consider that the *trans* isomer was yielded exclusively in the case of the bis-(2,6-dimethylpyridine) complex, since the *cis* isomer is quite unfavorable because of the steric hindrance of the methyl substituents. The methyl proton signal of the coordinated 2,6-dimethylpyridine is observed as a sharp singlet at 6.62 τ, shifting towards the down-field side by *ca.* 1 τ on ligation. The free ligand added to this solution causes absorption at 7.48 τ, indicating no sign of the ligand exchange.

The spectrum of the 2-methylpyridine complex **4b** exhibits a different pattern. The two peaks observed at 7.48 and 6.93 τ are assigned to the $CH_2^{(a)}$ and $CH_2^{(b)}$ protons, indicating that the complex has the *trans* configuration just as in the case of the 2,6-dimethylpyridine complex. The benzyl methylene protons are observed as two separate peaks at 4.93 and 4.88 τ in the area ratio 3:7. A slight splitting of the $CH_2^{(b)}$ signal can be seen in the 100 MHz spectrum. In the case of the corresponding 2-ethylpyridine complex, the $CH_2^{(b)}$ protons afford two distinct peaks; the area ratio for $CH_2^{(b)}$ signals at 7.00 and 6.95 τ and that for $CH_2^{(c)}$ signals at 4.96 and 4.88 τ are both 3:7. Since the $CH_2^{(a)}$ signal shows no splitting in either case, these features do not suggest the coexistence of *cis* isomers, but seem to indicate that the $CH_2^{(c)}$ and even $CH_2^{(b)}$ protons can occupy two non-equivalent positions.

Splitting of the $CH_2^{(c)}$ and $CH_2^{(b)}$ proton signals is not observed for complexes of symmetric bases such as pyridine, 4-methyl- and 2,6-dimethyl-pyridines, but appears only in the spectra of unsymmetrically 2-substituted pyridine complexes. Steric hindrance for the free rotation of 2-substituted pyridine ligands about the M–N bond in palladium(II)[13)] and platinum(II)[14)]

complexes has been well documented by studies of variable-temperature NMR spectra. For the present 2-methylpyridine complex **4b** also locked structures might be assumed in which the pyridine rings are fixed perpendicular to the coordination plane of palladium(II). Two conformations are considered; (a) methyl groups of the two 2-methylpyridine ligands exist on the same side of the coordination plane (syn), and (b) they lie on the opposite sides of the square plane (anti). The spectrum of $PdCl(CH_2COCH_2COOCH_2Ph)(2\text{-Et-py})_2$ exhibits a multiplet centered at 8.5 τ which is slightly more complicated than a double-triplet, and another multiplet (nearly double-quartet) at 6.34 τ. These resonances are assigned to the methyl and methylene protons of the ethyl group attached to pyridine, respectively, and seem to disclose the coexistence of the locked syn and anti structures.

Splitting of the $CH_2^{(c)}$ and $CH_2^{(b)}$ proton signals of the 2-alkylpyridine complexes might be related to such a relative conformation of the two pyridine ligands, although the exact locked structure of the dangling benzyl ester ligand is not certain. The reason why the $CH_2^{(a)}$ protons give a single resonance is not clear either, but the rotation of the ester ligand about the Pd–C bond might equal the averaged magnetic circumstances of $CH_2^{(a)}$ protons in the syn and anti configurations.

Substitution of Pyridine Ligands with Other Pyridines. In order to find the relative stability of the complexes containing various pyridine derivatives, substitution of the pyridine ligands with other pyridines was examined. Qualitative results were obtained by substitution reactions for several hours at room temperature, and reveal some interesting features (Table 4).

Table 4. Substitution of pyridine ligands L in $PdCl(CH_2COCH_2COOCH_2C_6H_5)L_2$ with other pyridine derivatives L′ in dichloromethane at room temperature[a)]

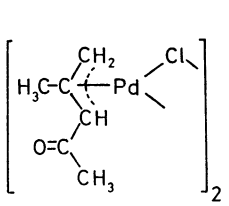
L′ / L =	py	2-Me-py	4-Me-py	2,6-Me_2-py	bipy
py	—	○	○	×	×
2-Me-py	○	—	○	×	×
4-Me-py	○	○	—	×	×
2,6-Me_2-py	×	×	×	—	×
bipy	○	○	○	○	—

a) ○ indicates the replacement of the ligand L by L′. × indicates no reaction, the starting complex being recovered.

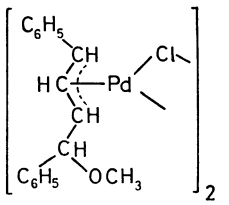
Unsubstituted, 2-methyl-, and 4-methyl-pyridines show similar behavior, being interchangable with each other. The bis(2,6-dimethylpyridine)-complex is very stable, the ligand not being displaced by the other unidentate pyridines. The inertness for substitution reactions can be ascribed to steric shielding of the metal atom by the *ortho*-substituents in the pyridine ligand. On the other hand 2,6-dimethylpyridine is very weak as an attacking nucleophile. It can not substitute any pyridine ligand coordinated to palladium(II). The *ortho*-substituents might retard the nitrogen atom to approach the metal atom. 2,2′-Bipyridine is the most powerful ligand. It can displace any unidentate pyridines in the coordination sphere; once it is bonded to palladium(II), it is not replaced by any unidentate pyridines. Such extraordinary stability must be due to the chelate effect.

Supplementary Discussion. The currently favored mechanism for the syn-anti isomerization in π-allyl complexes involves a σ-bonded intermediate.[15)] π-Allylpalladium(II) complexes have also been widely suggested as intermediates in various catalytic reactions.[16)] The conversion of π-allyl into σ-allyl can usually be detected by NMR-spectral observations. Only a few reports have appeared on the isolated σ-allyl palladium(II) compounds.[17)]

In the present reactions the starting π-allylic complexes gave stable σ-alkyl palladium(II) compounds. However, the σ-2-hydroxyallyl moiety was not retained, but the accompanying tautomeric transformation caused the terminal-carbon-bonded acetoacetate-ester complexes. Similar π-allyl complexes **6**[18,19)] and **7**[20)] react with bases such as pyridine and triphenylphosphine to afford monomeric complexes, but the σ-allylic complexes are not stable enough to be isolated. These results suggest that the neighboring carbonyl group plays some role of stabilizing the σ-carbon bonding.



[6]



[7]

Both the chelating acetylacetonate ligand and π-allylic acetoacetate-ester ligand can be converted into the σ-carbon bonding to palladium(II). However, the former prefers central carbon bonding, and the latter terminal-carbon bonding. This might be due to certain electronic and/or steric factors. The terminal-carbon bonding of a β-dicarbonyl compound to a transition metal has not yet been reported, but $TeCl_2(acac)_2$, obtained as a by-product in the reaction of tellurium(IV) chloride with acetylacetone, was found to be of such a bonding type.[21)] In contrast to the present palladium(II) complex, the acetylacetonate ligand in this tellurium(IV) complex has the enol (hydrogen chelate) form.

Experimental

π-Allylic Palladium(II) Complexes of Acetoacetate Esters. The ethyl acetoacetate complex, di-μ-chlorobis(π-1-ethoxycarbonyl-2-hydroxyallyl)dipalladium(II) [**1**] was synthesized according to Tezuka *et al.*[3)] The corresponding benzyl acetoacetate complex, di-μ-chlorobis(π-1-benzyloxycarbonyl-2-hydroxyallyl)dipalladium(II) [**2**] was prepared by adding diketene dropwise to a dichloromethane solution (12 ml) of dichlorobis(benzonitrile)palladium(II) containing 2 ml of benzyl alcohol at 0 °C. Dark red color of the solution faded gradually and a yellow precipitate appeared in 10—20 min. The product was filtered and washed repeatedly with petroleum ether. Yield: 0.67 g, 81%. Found: C, 39.55; H, 3.40%. Calcd for $C_{11}H_{11}O_3ClPd$: C, 39.66; H, 3.32%.

Tetrahydrofuran and dichloromethane are suitable solvents for recrystallization. Crude products were used without recrystallization in the following reactions.

Reaction of π-Allylic Palladium(II) Complexes of Acetoacetate Ester **1** *and* **2** *with Pyridine or Its Derivatives.* Pyridine (2—3 ml) was added with stirring to a suspension of the ethyl ester compex (0.7 g) in benzene (10 ml). The mixture turned immediately to a clear yellow-green solution. Petroleum ether was added to this solution to separate the precipitate. Yield: 1.0 g, 91%. The product was dissolved in dichloromethane and recrystallized by addition of petroleum ether. The other reaction of π-allylic palladium(II) complexes of acetoacetate esters with pyridine derivative were performed in a similar way, affording the following yields: **3b**, 82%; **4a**, 82%; **4b**, 84%; **4c**, 96%; **4d**, 94%; **4e**, 95%.

The monomeric intermediate chloro(pyridine) (π-1-benzyloxycarbonyl-2-hydroxyallyl)palladium(II) [5] was isolated in the following way. Pyridine (0.043 g, 0.54 mmol) was added to a suspension of the starting benzyl-ester complex **2** (0.177 g, 0.53 mmol) in dichloromethane. The resulting clear solution was evaporated to dryness, and the residue was extracted with benzene to remove the final carbon-bonded product **4a**. The remaining residue was then extracted with dichloromethane to obtain the π-allylic monomer **5** in a 45% yield. Found: C, 46.21; H, 3.50; N, 3.30%. Calcd for $C_{16}H_{16}NO_3ClPd$: C, 46.62; H, 3.91; N, 3.39%. Molecular weight could not be determined, since **5** was unstable in solution and readily disproportionated into the dimeric parent complex **2** and the final carbon-bonded bis(pyridine) complex **4a**.

Substitution of Pyridine Ligands with Other Pyridines. To a solution of each complex in dichloromethane, an excess amount of another free ligand was added and allowed to react for 3—4 hr. Petroleum ether was then added to this solution to separate the palladium(II) complex, which was identified by the IR assay.

Measurements. Infrared spectra were measured with JASCO IR-E (4000—600 cm^{-1}) and Hitachi grating EPI-L spectrophotometers. The NMR spectra were recorded at 60 MHz with tetramethylsilane as an internal reference on JEOL C60-HL and PS-100 spectrometers. The molecular weight was determined in dichloromethane at 25 °C by means of vapor pressure osmometry with an apparatus manufactured by Knauer, Germany.

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