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O,O'-Chelate and Central-Carbon-Bonded Complexes of Ethyl Acetoacetate with Palladium(II)

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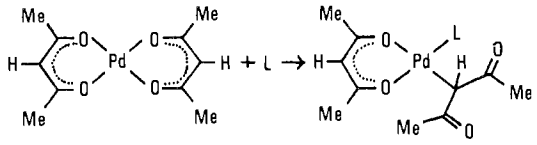
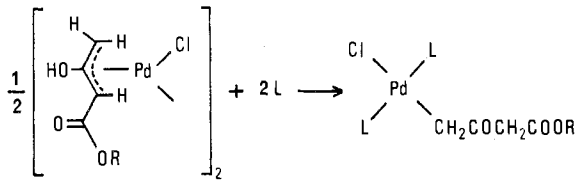
The reaction of ethyl acetoacetate (etacH) with sodium tetrachloropalladate(II) in aqueous alkaline solution afforded a yellow compound of the formula $Pd(etac)_2 \cdot {}^1/_2H_2O$ [1]. The key intermediate **1** turns spontaneously into the bis-*O,O'*-chelate Pd(etac-*O,O'*)$_2$ [2] in dichloromethane, whereas **1** reacts with excess nitrogen bases in appropriate solvents to yield the central-carbon-bonded complexes Pd(etac-C^2)$_2$L$_2$ [3], where L is pyridine, 2-methylpyridine, benzylamine, or *n*-butylamine. When compound **3** is dissolved in chloroform, one L is liberated to result in Pd(etac-*O,O'*)(etac-C^2)L [4], which is also produced by the reaction of **2** with an equimolar amount of L. Each of these complexes has cis and trans isomers, which were characterized in solution by the proton NMR spectroscopy.

Acetylacetone and other β-dicarbonyl compounds[2] are very versatile ligands exhibiting various modes of bonding to metal ions.[3] Most usually the acetylacetonate anion coordinates to a metal ion via the two oxygen atoms, forming a six-membered chelate ring.[4] The unidentate linkage via the central carbon atom is also well-known for platinum(II) and other rather soft metal ions.[5] Recently bis(acetylacetonato)palladium(II) was found to react with Lewis bases (L) such as triphenylphosphine, pyridine, diethylamine, and *N*-methylbenzylamine to afford the first examples of the central-carbon-bonded palladium(II) complexes of acetylacetone, Pd(acac-*O,O'*)(acac-C^3)L.[6]



Although the bis-*O,O'*-chelates of ethyl acetoacetate with a few metal ions such as copper(II) and nickel(II) are known, the corresponding palladium(II) complex has not yet been reported, but the η-allylic complex di-μ-chloro-bis(η^3-1-ethoxycarbonyl-2-hydroxyallyl)dipalladium(II)[7] was obtained by the ethanolysis of diketene in the presence of tetrachloropalladate(II) or by the direct reaction of ethyl acetoacetate with palladium(II) chloride in water at 40–60 °C. The η-allylic complex reacts with pyridine and its derivatives (L) to afford the terminal-carbon-bonded complexes PdCl(CH$_2$COCH$_2$COOR)L$_2$.[8] The central-carbon-bonded product was not obtained at all in this case.



R = Et or CH_2Ph cis and trans

In order to discover the factors governing the bonding modes of the β-dicarbonyl ligands to palladium(II), it is desirable to prepare the complexes containing a particular ligand in different linkage forms and to investigate the transformations among them. The present paper reports the preparation and characterization of the *O,O'*-chelate and the central-carbon-bonded complexes of ethyl acetoacetate with palladium(II).

Experimental Section

The Intermediate Complex of the Composition $Pd(etac)_2 \cdot {}^1/_2H_2O$ [1]. Ethyl acetoacetate (3.3 mL, 25 mmol) was added to an aqueous solution (25 mL) of Na_2PdCl_4 (12.5 mmol). An aqueous solution (5 mL) of KOH (25 mmol) was added to this solution with vigorous stirring to deposit red resinous solid on the wall. The solution was decanted and the residue was triturated with water to transform it into a tractable yellow powder, which was filtered, washed with methanol followed by ether, and dried in vacuo. The yield was 61% (2.86 g).

Bis(ethyl acetoacetato)palladium(II), Pd(etac-*O,O'*)$_2$ [2]. A suspension of complex **1** (890 mg) in dichloromethane (100 mL) was stirred for several hours at room temperature to result in a yellow solution. After filtration, petroleum ether (100 mL) was added to the filtrate and the mixed solvent was allowed to evaporate spontaneously at room temperature. The light brown microcrystals which deposited on the wall were recrystallized from dichloromethane–petroleum ether. The yield was 64% (553 mg).

Bis(1-ethoxycarbonylacetonato-C^1)bis(pyridine)palladium(II) Semihydrate, Pd(etac-C^2)$_2$(py)$_2 \cdot {}^1/_2H_2O$ [3a]. Complex **1** (206 mg) was dissolved in pyridine (1 mL), and ether was added to the solution to precipitate yellow crystals in a 72% yield (210 mg). By using 2-methylpyridine instead of pyridine, yellow plates of Pd(etac-C^2)$_2$(2-Mepy)$_2$ [3b] were obtained in an 80% yield.

Bis(1-ethoxycarbonylacetonato-C^1)bis(benzylamine)palladium(II), Pd(etac-C^2)$_2$(PhCH$_2$NH$_2$)$_2$ [3d]. To a suspension of complex **1** (455 mg, 1.2 mmol) in ether (several milliliters) was added benzylamine (0.5 mL, 4.6 mmol) dropwise with stirring to afford a yellow solution. Petroleum ether was added and the mixture was cooled to deposit yellow needles in a 67% yield (483 mg).

Bis(1-ethoxycarbonylacetonato-C^1)bis(*n*-butylamine)palladium(II), Pd(etac-C^2)$_2$(*n*-BuNH$_2$)$_2$ [3e]. To a suspension of complex **1** (163 mg, 0.44 mmol) in benzene (several milliliters) was added *n*-butylamine (0.5 mL, 5.0 mmol) dropwise with stirring to give a yellow solution. Petroleum ether was added and the solution was cooled to deposit yellow needles in a 42% yield (94 mg).

Bis(1-ethoxycarbonylacetonato-C^1)(2,2'-bipyridine)palladium(II), Pd(etac-C^2)$_2$(bpy) [3f]. To a solution of complex **3a** (64 mg, 0.12 mmol) in dichloromethane (0.5 mL) was added 2,2'-bipyridine (25 mg, 0.16 mmol), followed by a small portion of petroleum ether, and the mixed solvent was allowed to evaporate spontaneously at room temperature. Yellow crystals were obtained in the quantitative yield (64 mg).

(Ethyl acetoacetato)(1-ethoxycarbonylacetonato-C^1)(2,6-dimethylpyridine)palladium(II), Pd(etac-*O,O'*)(etac-C^2)(2,6-Me$_2$py) [4c]. Complex **2** (28.7 mg, 0.08 mmol) was dissolved in dichloromethane (0.5 mL) containing 2,6-dimethylpyridine (18 mg, 0.17 mmol). Petroleum ether (3 mL) was added to the solution and the mixed solvent was allowed to evaporate spontaneously to afford yellow crystals in a 67% yield (25 mg).

(Ethyl acetoacetato)(1-ethoxycarbonylacetonato-C^1)(benzylamine)palladium(II), Pd(etac-*O,O'*)(etac-C^2)(PhCH$_2$NH$_2$) [4d], was also prepared in dichloromethane by the reaction of **2** with benzylamine in a 6% yield.

(Acetylacetonato-*O,O'*)(acetylacetonato-C^3)(2-, 3-, or 4-methylpyridine)palladium(II), Pd(acac-*O,O'*)(acac-C^3)(2-, 3-, or 4-Mepy). The compound Pd(acac-*O,O'*)(acac-C^3)py (125 mg), which was prepared by the reaction of Pd(acac)$_2$ with pyridine,[6] was dissolved in 2-methylpyridine on heating. Petroleum ether and ethyl ether were added to the solution and cooled to separate out yellow crystals. The

Table I. Analytical Data of Palladium(II) Complexes

No.	Complex	% calcd (found) C	H	N	Mol wt[a] calcd (found)	Dec pt, °C
1	$Pd(etac)_2 \cdot {}^1/_2 H_2O$	38.57 (38.41)	5.13 (4.92)			134
2	Pd(etac-*O*,*O*′)$_2$	39.52 (39.51)	4.98 (5.01)		365 (343)	126
3a	Pd(etac-C^2)$_2$(py)$_2 \cdot {}^1/_2 H_2O$	49.68 (49.95)	5.50 (5.51)	5.27 (5.29)		99
3b	Pd(etac-C^2)$_2$(2-Mepy)$_2$	52.32 (52.20)	5.86 (5.86)	5.08 (5.00)	551 (276)	84
3d	Pd(etac-C^2)$_2$($PhCH_2NH_2$)$_2$	53.93 (53.85)	6.27 (6.31)	4.84 (4.74)	579 (356)	124
3e	Pd(etac-C^2)$_2$(*n*-$BuNH_2$)$_2$	46.99 (46.85)	7.95 (7.87)	5.48 (5.46)	511 (355)	109
3f	Pd(etac-C^2)$_2$(bpy)	50.73 (51.16)	5.03 (5.27)	5.38 (5.13)		201
4c	Pd(etac-*O*,*O*′)(etac-C^2)(2,6-Me_2py)	48.36 (48.44)	5.77 (5.79)	2.97 (3.04)	472 (457)	113
4d	Pd(etac-*O*,*O*′)(etac-C^2)($PhCH_2NH_2$)	48.36 (48.37)	5.77 (5.77)	2.97 (2.89)		109
	Pd(acac-*O*,*O*′)(acac-C^3)(2-Mepy)	48.31 (48.06)	5.32 (5.32)	3.52 (3.39)		125
	Pd(acac-*O*,*O*′)(acac-C^3)(3-Mepy)	48.31 (48.00)	5.32 (5.26)	3.52 (3.60)		90
	Pd(acac-*O*,*O*′)(acac-C^3)(4-Mepy)	48.31 (48.36)	5.32 (5.32)	3.52 (3.50)		100
	Pd(acac-*O*,*O*′)(acac-C^3)(3,5-Me_2py)	49.58 (49.82)	5.63 (5.76)	3.40 (3.73)		123

[a] Determined in $CHCl_3$ at 34 °C except for **2** (at 42 °C).

corresponding 3- and 4-methylpyridine complexes were prepared by the direct reactions of $Pd(acac)_2$ with pyridines. The yields were 45, 20, and 35% for the 2-, 3-, and 4-methylpyridine complexes, respectively.

(Acetylacetonato-*O*,*O*′)(acetylacetonato-C^3)(3,5-dimethylpyridine)palladium(II), Pd(acac-*O*,*O*′)(acac-C^3)(3,5-Me_2py). To a dichloromethane solution of Pd(acac-*O*,*O*′)(acac-C^3)py was added 3,5-dimethylpyridine, and the solvent was allowed to evaporate spontaneously in a refrigerator to deposit orange-yellow crystals in the quantitative yield.

Measurements. Infrared spectra were obtained with Hitachi EPI-S2 (4000–700 cm^{-1}) and EPI-L (700–200 cm^{-1}) infrared spectrophotometers. Proton NMR spectra were recorded at 60 MHz on a JNM C-60 HL instrument using TMS as an internal reference and $CDCl_3$ as a solvent. The molecular weight was determined with a vapor pressure osmometer manufactured by Knauer, Berlin, Germany.

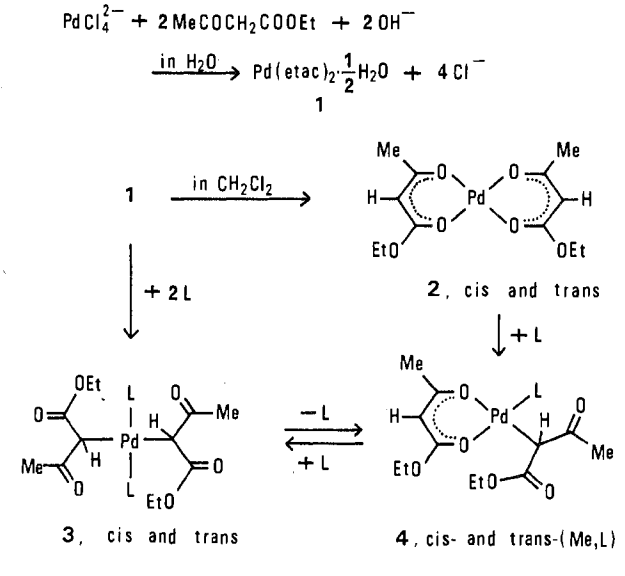
Results and Discussion

Sodium tetrachloropalladate(II) reacts with twice as many moles of ethyl acetoacetate in aqueous solution containing twice the moles of potassium hydroxide to afford a key intermediate **1** of the composition $Pd(etac)_2 \cdot {}^1/_2 H_2O$. Compound **1** converts spontaneously to the bis-*O*,*O*′-chelate Pd(etac-*O*,*O*′)$_2$ [**2**] in dichloromethane, whereas it reacts with an excess amount of a base (L) to give the complex Pd(etac-C^2)$_2$L$_2$ [**3**] in a high yield, where L is pyridine [**3a**], 2-methylpyridine [**3b**], benzylamine [**3d**], or *n*-butylamine [**3e**]. A similar bipyridine complex [**3f**] is conveniently prepared by the ligand substitution reaction of the pyridine complex **3a** with 2,2′-bipyridine. These complexes are the first examples of a palladium(II) complex containing two β-dicarbonyl ligands coordinated through the central carbon atom, although the corresponding anionic platinum(II) complexes $Na_2[PtCl_2(acac\text{-}C^3)_2]$ and K[Pt(acac-*O*,*O*′)(acac-C^3)$_2$] are well-known.[9] The central-carbon bonding of ethyl acetoacetate in the present complexes was established on the IR and NMR spectra and ascertained by the x-ray analysis of complex **3b**.[10] This type of bonding of ethyl acetoacetate was first observed by Hazell and Truter[11] in $[Pt(CH_3)_3(etac)]_2$ where the ester acts as a bridging ligand.

When a compound **3** is dissolved in chloroform, one of the central-carbon-bonded ester ligands turns to the *O*,*O*′-chelate, liberating one L concurrently to result in Pd(etac-*O*,*O*′)(etac-C^2)L [**4**]. Complexes of the same type are also derived from **2** by the reaction with an equimolar amount of L, and crystalline products were isolated when 2,6-dimethylpyridine and benzylamine were used as L. These reactions are summarized in Scheme I, and the analytical data of the isolated complexes are listed in Table I.

The bonding mode of ethyl acetoacetate is easily diagnosed on the basis of the spectral pattern in the 1500–1700-cm^{-1} region. Three bands observed in the 1510–1607-cm^{-1} region are assigned to the $\nu_s(C{=}O) + \nu_{as}(C{=}C{=}C)$ vibrations of the *O*,*O*′-chelate,[12] while two bands in the 1620–1716-cm^{-1} region

Scheme I



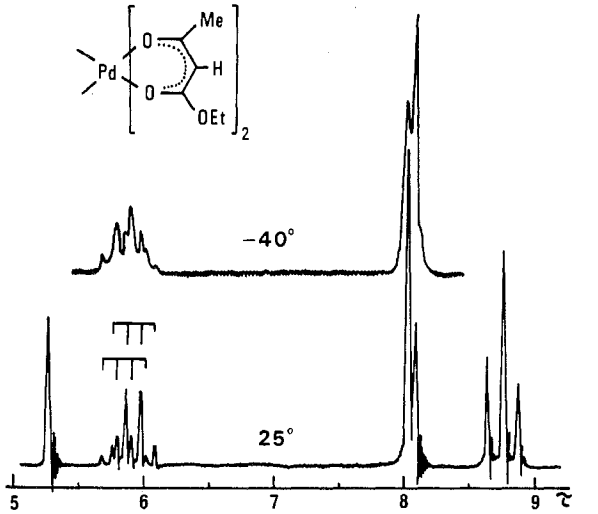
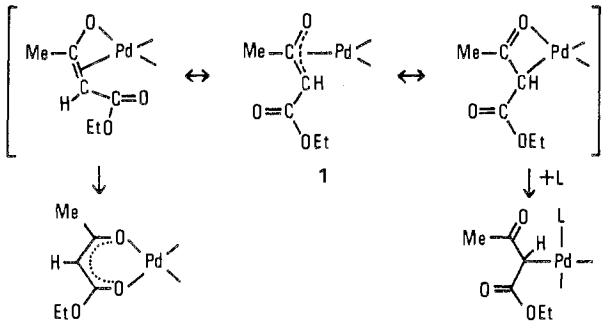


Figure 1. Proton NMR spectra of Pd(etac-*O*,*O*′)$_2$ in $CDCl_3$ at +25 and −40 °C immediately after dissolution.

are assigned to the $\nu(C{=}O)$ of the central-carbon-bonded ligand.[13] The band observed at 550–570 cm^{-1} solely for complexes containing the carbon-bonded ester ligand is attributed to the $\nu(Pd{-}C)$ vibration by reference to the data of the corresponding acetylacetonate complexes.[6]

The Intermediate Complex 1. Compound **1** exhibits strong bands at 1710 and 1560 cm^{-1} together with weak ones at 1600

and 1515 cm^{-1}, the spectral pattern being different from that of an *O,O'*-chelate. It cannot be considered to contain the central-carbon-bonded or terminal-carbon-bonded ligand[8] either, since no absorption assignable to the ν(Pd–C) vibration is observed in the 500–600-cm^{-1} region. Upon dissolution in dichloromethane compound **1** turns to the bis-*O,O'*-chelate, while in pyridine both of the ester ligands are transformed into the central-carbon-bonded state. These facts suggest that the compound **1** may have a structure which is easily convertible into either of the *O,O'*-chelated and central-carbon-bonded states. Although further characterization of **1** is difficult at the present stage of investigation, we tentatively assume the η-oxopropenyl coordination of the ester ligand to palladium(II) in **1**



Similar η-oxopropenyl coordination was presumed for intermediates in the hydrogenation of α,β-unsaturated carbonyl compounds catalyzed by cobalt and iron hydridocarbonyls[14] and also in the decarbonylation of saturated aldehydes by a ruthenium complex.[15] Recently the reaction of dichlorobis(benzonitrile)palladium(II) with diazoacetophenone or diazoacetone in dichloromethane was reported to afford di-μ-chloro-bis(2-phenyl(or methyl)-3-chloro-η-oxopropenyl)-dipalladium(II),[16] and the molecular structure of 1-(*o*-diphenylphosphinophenyl)-1,2-dimethyl-η-oxopropenylmanganese(I) tricarbonyl was determined by x-ray analysis.[17]

Bis(ethyl acetoacetato)palladium(II) [2]. The infrared spectrum of compound **2** bears a close resemblance to that of bis(ethyl acetoacetato)copper(II),[18] certifying the *O,O'*-chelation of the ester ligands in **2**. Proton NMR spectra displayed in Figure 1 also support the chelate structure in **2**. Although the terminal methyl CH_2CH_3 and methine CH protons exhibit one kind of triplet and singlet signals at τ 8.76 (J = 7 Hz) and 5.26, respectively, the acetyl methyl $COCH_3$ and methylene CH_2 protons show two kinds of singlets (τ 8.03 and 8.09) and quartets (τ 5.85 and 5.92), respectively. The spectral behavior seems to suggest the coexistence of cis and trans isomers in the bis-*O,O'*-chelate of ethyl acetoacetate. It is very interesting that the central methine and the farthest methyl protons are insensitive to the difference in the geometrical structure around the metal, whereas the acetyl methyl and methylene groups reflect the environmental difference.

Hendrickson and Martin[19] characterized the cis and trans isomers of nickel triad complexes of *O*-ethyl thioacetothioacetate. The NMR spectra of palladium(II) and platinum(II) complexes in C_6D_6 are quite similar to those in Figure 1. By reference to their assignment the more intense of the two acetyl methyl signals at lower field (Figure 1) is ascribed to the trans isomer. As is seen in Figure 1, the spectrum in $CDCl_3$ at −40 °C shows predominance of the cis isomer immediately after dissolution but shortly changes to the equilibrium pattern corresponding to the ratio 7:3 of trans and cis. Crystals of **2** seem to have an abundance of the cis form, which on dissolution in chloroform isomerizes quickly to the more favorable trans form. The equilibrium composition of isomers does not change with temperature, and the broadening of signals was not observed up to 60 °C.

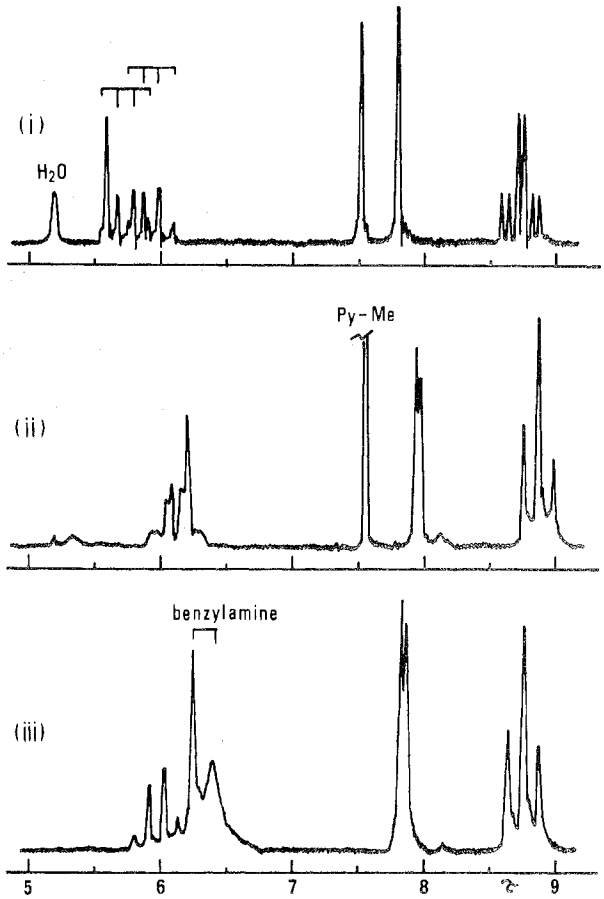


Figure 2. Proton NMR spectra of (i) *cis*-Pd(etac-C^2)$_2$(py)$_2$·$^1/_2H_2O$ and (ii) *trans*-Pd(etac-C^2)$_2$(2-Mepy)$_2$ in pyridine and of (iii) *trans*-Pd(etac-C^2)$_2$($PhCH_2NH_2$)$_2$ in $CDCl_3$ containing 3 molar excess of $PhCH_2NH_2$. Spectra were measured at 25 °C immediately after dissolution.

The stereochemical transformation of the octahedral tris chelates of unsymmetric β-dicarbonyl compounds has been studied quite extensively mainly by means of the variable-temperature NMR spectroscopy.[20] The square-planar bis chelates of similar ligands also have trans and cis isomers, but neither the isolation of the isomeric pairs nor the characterization of them in solution has been reported so far. Recently we have isolated *cis*- and *trans*-bis(benzoylacetonato)palladium(II) and determined the x-ray structure of the cis isomer.[21] Analogous palladium(II) complexes of other unsymmetric β-dicarbonyl compounds are also under investigation.

Bis(1-ethoxycarbonylacetonato-C^1)bis(base)palladium(II) [3]. By dissolving compound **1** in pyridine or 2-methylpyridine, Pd(etac-C^2)$_2$(py)$_2$·$^1/_2H_2O$ [**3a**] and Pd(etac-C^2)$_2$(2-Mepy)$_2$ [**3b**] were obtained, respectively. Similarly the reactions of **1** with benzylamine and *n*-butylamine in appropriate solvents yielded complexes **3d** and **3e** of the corresponding compositions. As is shown by the infrared data, these compounds contain two carbon-bonded ester ligands together with two nitrogen bases, and hence they may have cis and trans isomers.

Immediately after dissolution of **1** or **3a** in pyridine at 25 °C, the NMR spectrum (i) in Figure 2 is observed, but another spectrum (ii) grows up gradually with time in the expense of (i). After about 20 h spectra (i) and (ii) attain an equilibrium with the intensity ratio of 2:1, indicating coexistence of cis and trans forms. On the other hand a fresh solution of Pd(etac-C^2)$_2$(2-Mepy)$_2$ [**3b**] in pyridine gives spectrum (ii) together with a peak assignable to methyl protons of liberated 2-methylpyridine, showing that the 2-methylpyridine ligand

Table II. Proton NMR Spectra of Pd(etac-C^2)$_2$L$_2$ Complexes at 25 °C[a]

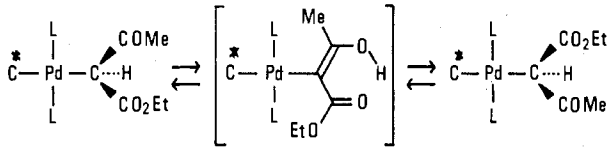
L	Solvent	Geometry	$COCH_3$	CH	CH_2CH_3	CH_2CH_3
py	py	Cis	7.80, 7.52	5.59	5.92, 5.73	8.76, 8.71
		Trans	7.97, 7.94	6.20	6.14, 6.11	8.87
	$CDCl_3$	Cis[b]	8.05, 7.83	6.00		8.75, 8.66
		Trans[c]	8.17, 8.14	6.42	6.07, 6.03	8.84
2-Mepy	CD_2Cl_2[d]	Trans	8.55, 8.41	6.72, 6.65	6.30, 6.20	8.88, 8.86
$PhCH_2NH_2$	$CDCl_3$[e]	Trans	7.87, 7.84	(6.2-6.5)	5.97	8.77

[a] Chemical shifts in τ at 60 MHz with internal TMS. The area ratio of split signals is 1:1 in either case. $J_{CH_2\text{-}CH_3}$ = 7 Hz. [b] Observed as rapidly diminishing signals immediately after dissolution of **3a** in $CDCl_3$. The CH_2 signal is masked by the growing peak of **4a**. [c] Observed when excess pyridine was added to a solution of **2** in $CDCl_3$. [d] Measured at −50 °C. [e] Three molar excess of benzylamine was added to prevent the ligand dissociation. The CH signal is hidden by the CH_2 signal of benzylamine.

is instantaneously substituted by pyridine. In this case spectrum (i) grows with time to attain the same equilibrium as above.

These spectral behaviors clearly demonstrate that the predominant isomers existing in fresh solutions of **3a** and **3b** in pyridine are different from each other. Spectrum (ii) may be attributed to *trans*-Pd(etac-C^2)$_2$(py)$_2$ since crystals of **3b** are composed of *trans*-Pd(etac-C^2)$_2$(2-Mepy)$_2$ molecules,[10] and the geometrical configuration is usually retained in the ligand substitution of square-planar complexes.[22] Then spectrum (i) may be assigned to *cis*-Pd(etac-C^2)$_2$(py)$_2$, and crystals of **3a** are considered to be composed of cis molecules.

Each signal except that for CH in spectrum (i) in Figure 2 is split into two parts of equal intensity. The central carbon atom of the ester ligand linked to palladium is asymmetric, and the complex molecule can be either an *RR*(*SS*) or an *RS* diastereoisomer. The 1:1 splitting of proton signals seems to reflect coexistence of the two diasteromers in equal proportions. Similar splitting of proton signals is also observed in spectrum (ii) of the trans isomer, but the extent of splitting is much smaller than that in spectrum (i) of the cis isomer probably because the separation between the two asymmetric centers is larger in trans than in cis. The crystal of **3b** is racemic involving an equal number of *RR* and *SS* diastereomers.[10] The transformation of *RR*(*SS*) into *RS* to attain an equilibrium in pyridine at room temperature is accomplished during about 5 min which is required for sample preparation. The mechanism of this rather fast interconversion is not clear, but the following unimolecular tautomeric process might be responsible



The methine proton is in fact very labile and is completely exchanged within 5 min by D_2O added in pyridine solution. However the spectral pattern is maintained up to 90 °C with no sign of coalescence, indicating that the interconversion between diastereomers is slow on the NMR time scale.

The NMR spectra of Pd(etac-C^2)$_2$L$_2$ complexes are listed in Table II. When compound **3a** is dissolved in $CDCl_3$, one molecule of pyridine is liberated to produce **4a**. NMR signals diminishing concomitantly in this process were attributed to the spectrum of *cis*-Pd(etac-C^2)$_2$(py)$_2$ in $CDCl_3$. On the other hand, when excess pyridine is added to a solution of Pd(etac-*O*,*O*′)$_2$ [**2**] in $CDCl_3$, NMR signals similar to (ii) in Figure 2 appear gradually. These were ascribed to *trans*-Pd(etac-C^2)$_2$(py)$_2$ in $CDCl_3$. The spectrum of *trans*-Pd(etac-C^2)$_2$(2-Mepy)$_2$ [**3b**] in CD_2Cl_2 was measured at −50 °C. The *RR*(*SS*) conformation in crystals seems to be retained in solution at the low temperature, but the spectrum exhibits signal splitting as is seen in Table II. Even the splittings of CH and ester CH_3 signals are observed which were absent in the spectrum of **3b** in pyridine at room temperature. Thus the splittings in the present case may be attributed to the coexistence of geometrical syn and anti isomers which have methyl groups attached to pyridine rings on the same or reverse side of the coordination plane, respectively. The signal of pyridine methyl protons is also split.

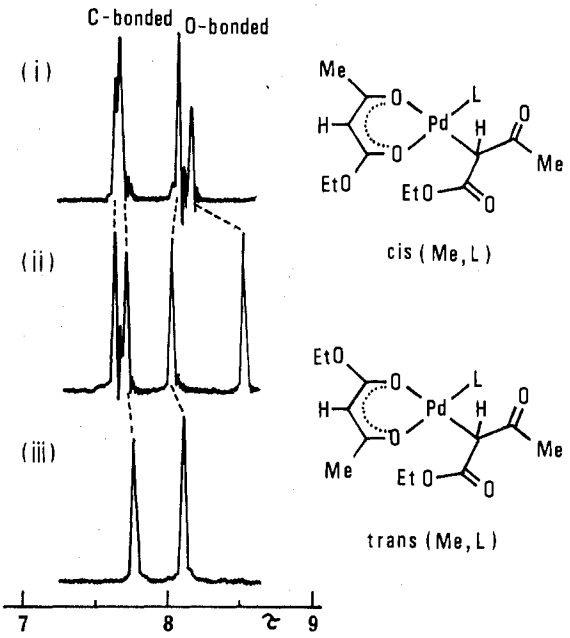


Figure 3. Acetyl methyl proton resonances of Pd(etac-*O*,*O*′)(etac-C^2)L in $CDCl_3$, where L = py (i), PPh_3 (ii), or $PhCH_2NH_2$ (iii).

The spectrum of the benzylamine complex **3d** was measured in $CDCl_3$ containing 3 times the molar amount of free amine to prevent the ligand dissociation. As is seen in Figure 2(iii) the signal splitting is small and the spectrum was assigned to the trans isomer. A good spectrum of the 2,2′-bipyridine complex [**3f**] could not been obtained because of its poor solubility and stability, but a fresh solution in $CDCl_3$ showed two $COCH_3$ signals at τ 7.60 and 7.50 in the intensity ratio of 1:1.

(Ethyl acetoacetato-*O*,*O*′)(1-ethoxycarbonylacetonato-C^1)(base)palladium(II) [4]. When Pd(etac-*O*,*O*′)$_2$ [**2**] is dissolved in $CDCl_3$ and allowed to react with an equimolar amount of a base (L), a composite proton NMR spectrum is observed which can be assigned to *cis*- and *trans*-(Me,L)-Pd(etac-*O*,*O*′)(etac-C^2)L [**4**] as is listed in Table III. The acetyl methyl signals in spectra of compounds **4** containing pyridine, triphenylphosphine, and benzylamine as L are reproduced in Figure 3. The upfield signals are assigned to acetyl methyl protons of the *O*,*O*′-chelated ligand, while the downfield ones are assigned to those of the C-bonded ester by reference to the literature.[6,9b]

In the spectra of pyridine and triphenylphosphine complexes (Figure 3(i) and (ii)), the acetyl methyl signals for both the *O*,*O*′-chelated and C-bonded ligands are split in two peaks,

Table III. Proton NMR Data for Pd(etac-*O*,*O*′)(etac-C^2)L and Pd(acac-*O*,*O*′)(acac-C^3)L in $CDCl_3$ at Room Temperature[a]

Pd(etac-*O*,*O*′)(etac-C^2)L

		O-Bonded etac				C-Bonded etac						
		CH_3	CH	CH_2——CH_3		CH_3	CH	CH_2——CH_3		py Me[c]		[cis]/
L	Geometry	s	s	q	t	s	s	q	t	s		[trans]
py	Cis	8.18	5.23	*b*	*b*	7.66	*b*	*b*	*b*			1/2
	Trans	8.08	5.23	*b*	*b*	7.68	5.98	*b*	*b*			
2-Mepy	Cis	8.26	5.30	5.83	8.76	7.69 7.65	*b*	*b*	*b*	6.92, 6.77	(7.47)	1/2
	Trans	8.10	5.30	6.29	8.95	7.63	*b*	*b*	*b*	6.92, 6.80		
3-Mepy	Cis	8.17	5.27	*b*	*b*	*b*	*b*	*b*	*b*	7.63 (7.72)		1/2
	Trans	8.09	5.27	*b*	*b*	7.67	6.03	*b*	*b*			
4-Mepy	Cis	8.19	5.28	*b*	*b*	7.69	*b*	*b*	*b*	7.63 (7.67)		1/2
	Trans	8.10	5.28	*b*	*b*	7.71	5.99	*b*	*b*			
2,6-Me_2py	Cis	8.23	5.25	6.13	8.80	7.55	6.45	5.80	8.74	6.74, 6.53	(7.48)	2/3
	Trans	8.06	5.25	6.24	8.93	7.59	6.53	6.13	8.82	6.74, 6.56		
										2-Me	5-Me	
2,5-Me_2py	Cis	8.26	5.43	*b*	*b*	*b*	*b*	*b*	*b*	6.98, 6.83	(7.54) 7.65 (7.77)	2/3
	Trans	8.11	5.43	*b*	*b*	*b*	*b*	*b*	*b*	6.98, 6.86		
PPh_3	Cis	8.54	5.31	*b*	*b*	7.64	6.83 d	*b*	*b*			1/1
	Trans	8.04	5.31	7.02	9.34	7.72	6.58 d	*b*	*b*			
$PhCH_2NH_2$	Trans	8.12	5.33	6.02	8.76	7.77	5.92	6.02	8.76			0/1

Pd(acac-*O*,*O*′)(acac-C^3)L

	O-Bonded acac			C-Bonded acac		
L	CH_3 (L cis) s	CH_3 (L trans) s	CH s	CH_3 s	CH s	py Me[c] s
2-Mepy	8.21	8.05	4.75	8.04, 7.87	5.84	6.91 (7.47)
3-Mepy	8.13	8.03	4.65	7.86	5.81	7.63 (7.72)
4-Mepy	8.13	8.02	4.67	7.84	5.97	7.61 (7.67)
3,5-Me_2py	8.12	8.03	4.68	7.85	5.83	7.68 (7.78)

[a] Chemical shifts in τ values at 60 MHz with internal TMS. $J_{CH_2\text{-}CH_3}$ = 7 Hz. s = singlet, d = doublet, t = triplet, q = quartet. [b] Not discernible due to overlapping. [c] Chemical shifts for free pyridines are given in parentheses.

of which the separation is larger in (ii) than in (i). The methyl group in the position cis to L is usually sensitive to the nature of L,[6] and the upfield one of the signals for the *O*,*O*′-chelated ligand is ascribed to the *cis*-(Me,L) isomer. The low-field one of the signals for the C-bonded ligand is then assigned to the *cis*-(Me,L) isomer on the basis of area ratio. The *cis*-(Me,L)/*trans*-(Me,L) isomer ratio in Table III was determined as the area ratio of the two methyl peaks for the *O*,*O*′-chelated ligand. In the case of benzylamine complex each of the methyl signals for the *O*,*O*′-chelated and C-bonded ligands appears as a single peak. The chemical shifts of these peaks correspond to those of the trans isomer. It is not yet unequivocally certain whether complex **4d** exists in solution solely as the trans isomer or the two isomers exhibit the identical chemical shifts by chance. The latter might be the case since the methyl groups of the *O*,*O*′-chelated ligand in Pd(acac-*O*,*O*′)(acac-C^3)-($PhCH_2NH_2$) resonate as a single peak.[23] On the other hand the platinum(II) complex of trifluoroacetylacetone (tfacH), $K[PtCl(tfac\text{-}O,O')(tfac\text{-}C^3)]\cdot 2H_2O$, was reported to exist as one isomer in acetone-d_6.[24]

The reaction of the bis-*O*,*O*′-chelate **2** with an equimolar base L to convert one of the ester ligands into the C-bonded state proceeds nearly quantitatively in $CDCl_3$ at 25 °C within several minutes for pyridine, monomethylpyridines, and benzylamine, 20 min for triphenylphosphine, and 1 h for 2,5-dimethylpyridine. However the reaction of **2** with 2,6-dimethylpyridine is very slow probably because of the steric hindrance of methyl groups in the entering ligand, demanding about 20 h for completion. It is a surprise that 3,5-dimethylpyridine fails to react with **2** in spite of the minor steric hindrance compared with 2,6-dimethylpyridine.

Complexes **4** containing methyl-substituted pyridines exhibit interesting behavior. Figure 4 shows proton NMR spectra of some complexes in the methyl resonance region. Just after dissolution of crystals of the 2,6-dimethylpyridine complex **4c** in $CDCl_3$, the signals marked with downward arrows in (i) are observed mainly, but those marked with upward arrows grow up with time in the expense of the former to attain the equilibrium pattern displayed in (i) after about 1 h. Thus the crystal of **4c** is considered to be composed of *trans*-(Me,L) molecules, which isomerize partly in solution to reach the equilibrium *trans*-(Me,L) $\rightleftarrows$ *cis*-(Me,L). It is not clear whether the isomerization proceeds according to the intermolecular or intramolecular mechanism although the former seems the case for Pd(tfac-*O*,*O*′)(tfac-C^3)py which isomerizes more rapidly on addition of pyridine.[23b] In either of the complexes **4**, the methyl signals for *cis*-(Me,L) and *trans*-(Me,L) isomers are all sharp up to 60 °C, indicating that the geometrical isomerization in $CDCl_3$ is not fast on the NMR time scale.

In the spectrum (i) in Figure 4 three downfield peaks are attributed to the methyl protons of 2,6-dimethylpyridine. The highest peak at τ 6.74 remains unchanged during the *trans*-(Me,L) → *cis*-(Me,L) isomerization process, showing that it is the overlapping signal of the two isomers. Thus the 2,6-Me_2 protons of the *cis*-(Me,L) isomer resonate at τ 6.74 and 6.53, while those of the *trans*-(Me,L) isomer resonate at τ 6.74 and 6.56, the splitting ratio being 1:1 for either isomer. The splitting of pyridyl methyl resonance may be interpreted in terms of the hindered rotation of the disubstituted pyridine. The carbon atom of the ester ligand attached to the metal atom is asymmetric as pointed out already. The most favorable conformation of the ester ligand seems to be that depicted in Figure 5 holding the O–Pd–C bond perpendicular to the paper plane. The pyridine ring stands perpendicular to the coordination plane, and the environments of the two methyl

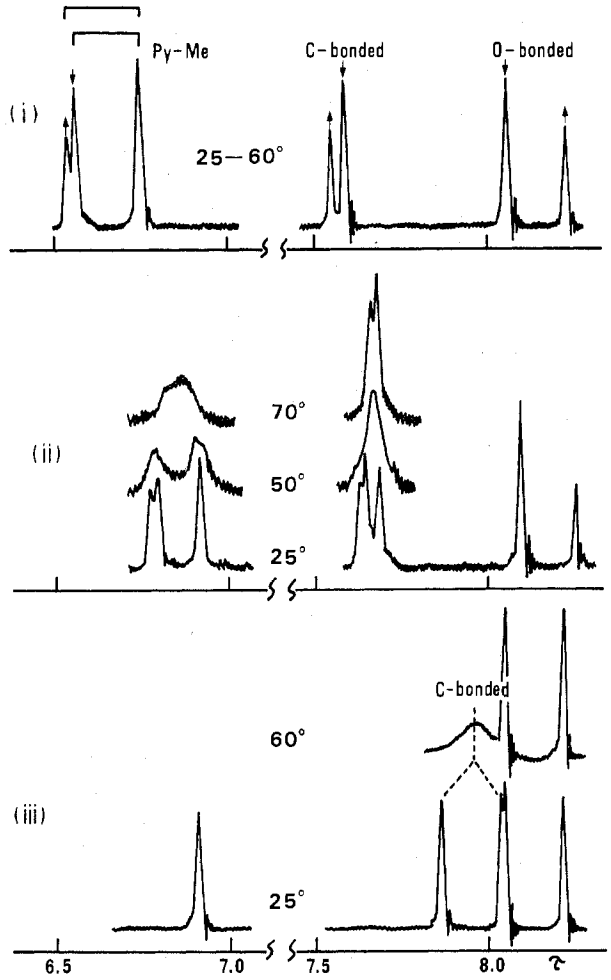


Figure 4. Acetyl and pyridyl methyl proton resonances of Pd(etac-*O*,*O*′)(etac-C^2)L with 2,6-Me_2py (i) or 2-Mepy (ii) as L and of Pd(acac-*O*,*O*′)(acac-C^3)(2-Mepy) (iii) in $CDCl_3$.

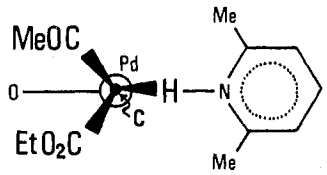


Figure 5. Ligand conformation in Pd(etac-*O*,*O*′)(etac-C^2)(2,6-Me_2py).

substituents are different. Signal broadening is not observed up to 60 °C, revealing that the barrier for the rotation around the Pd–N bond is high.

The situation for the 2-methylpyridine complex is quite similar to that for the 2,6-dimethylpyridine complex. Even if one of the two methyl substituents of the pyridine ligand in Figure 5 is replaced by a hydrogen atom, the environment of the remaining methyl group is different depending on whether it is situated above or below the coordination plane (in other words whether it is syn or anti with the acetyl group of the carbon-bonded ester ligand). Thus the four-line pattern is expected for the pyridyl methyl protons, but the observed spectrum (Figure 4(ii)) is quite similar to (i), the upfield resonances of cis and trans isomers overlapping by chance. As is shown in Figure 4(ii) the pyridyl methyl signals begin to broaden below 50 °C and collapse at 70 °C in sharp contrast to the case of the 2,6-dimethylpyridine complex for which no sign of broadening was observed up to 60 °C (Figure 4(i)). The difference in the spectral behavior reflects the situation that the rotation barrier for 2-methylpyridine is lower than that for 2,6-dimethylpyridine in these complexes. The three-line pattern is also observed for methyl protons of the carbon-bonded ester at 25 °C. The precise analysis is difficult, but it seems probable that the splitting is caused by the cis–trans isomerism together with the hindered rotation of 2-methylpyridine. (A four-line pattern is observed for a similar benzoylacetonate complex.[23b]) These signals collapse at about 50 °C and two peaks attributable to cis and trans isomers are clearly observed at 70 °C (Figure 4(ii)).

For the sake of comparison analogous acetylacetonato complexes Pd(acac-*O*,*O*′)(acac-C^3)L (L = 2-Mepy, 3-Mepy, 4-Mepy, 3,5-Me_2py) have been prepared and their NMR spectra examined. Figure 4(iii) displays the spectrum of Pd(acac-*O*,*O*′)(acac-C^3)(2-Mepy). Here again the cis and trans methyls of chelated acetylacetonate ligand with respect to L show different chemical shifts. On the other hand the two methyl signals for the carbon-bonded acetylacetonate are not caused by the cis and trans isomers but are assigned to the acetyl methyls which are syn and anti with the pyridyl methyl. In fact these two resonances collapse at about 60 °C, whereas those for the chelated acetylacetonate ligand remain sharp. The situation is quite the same as in the above-mentioned ethyl acetoacetate complex except that the environment of pyridyl methyl protons is not different in the two rotamers in this case.

When 3-methylpyridine is included as L, neither the acetylacetonato nor the ethyl acetoacetato complex shows the splitting of pyridyl methyl signals. The 3-methyl group seems to exert little steric hindrance rendering the rotation about the Pd–N bond almost free, since the signals of pyridyl H^2 and H^6 are not split. Furthermore, the 3-methyl group is so distant from the carbon-bonded β-dicarbonyl ligand that it does not influence the chemical shift of acetyl methyl protons even if the rotation of the pyridine ring is hindered. In fact no splitting of the acetyl methyl signals of Pd(acac-*O*,*O*′)(acac-C^3)(3-Mepy) is observed in CD_2Cl_2 even at −80 °C, and the 5-methyl signal of Pd(etac-*O*,*O*′)(etac-C^2)(2,5Me_2py) appears as a single peak at room temperature. Studies of hindered rotations of 2-methyl- and 2-chloromethylpyridines in square-planar d^8 complexes have been reported.[8,25] In the case of chloro(η-1,3-dimethylallyl)(2-methylpyridine)palladium(II), the free energy of activation for interconversion of syn and anti forms was estimated as 11.1 kcal/mol.[25a]

From Table III are omitted the NMR data of ring protons of the pyridine ligands. In the case of ethyl acetoacetato complexes the spectral pattern and chemical shifts of ring protons are quite similar to those of free ligands without showing any response to the *cis*- and *trans*-(Me,L) isomerism. The behavior of H^6 of the 2,5-dimethylpyridine complex is an exception. The signal splitting (τ 1.51 and 1.65) may again be rationalized in terms of the hindered rotation about the Pd–N bond. Although the chemical shifts of ring protons and 3-, 4-, and 5-methyl protons show only slight (<0.2 ppm) downfield shift by coordination, 2- and 6-methyl protons exhibit large downfield shifts of 0.5–1 ppm. Since the pyridine ring is perpendicular to the coordination plane and the 2- and 6-methyl protons are located in the proximity of the palladium atom, they may suffer some deshielding by the metal atom although not so much as observed in other palladium(II)[26] and -(0)[27] complexes.

Complementary Discussion

As described already, addition of an equimolar amount of a base L to a solution of **2** in chloroform affords complex **4**. The NMR spectra indicate that the reaction is quantitative for each L employed although the isolation of crystalline product was successful only when 2,6-dimethylpyridine and benzylamine were employed as L. The reverse reaction **4** → **2** could not be realized. On the other hand the reaction between **3** and **4** is generally reversible. If excess L is added

to the solution of **4** in chloroform, complex **3** is produced, and **3a**, **3b**, and **3d** containing pyridine, 2-methylpyridine, and benzylamine as L, respectively, were isolated in high yields. Conversely compound **3** dissociates one L to afford **4** in chloroform. (See eq 1.) The NMR assay indicates that **3a**

$$\underset{\mathbf{3}}{\mathrm{Pd(etac\text{-}}C^2)_2\mathrm{L}_2} \underset{+\mathrm{L}}{\overset{-\mathrm{L}}{\rightleftarrows}} \underset{\mathbf{4}}{\mathrm{Pd(etac\text{-}}O,O')(\mathrm{etac\text{-}}C^2)\mathrm{L}} \underset{+\mathrm{L}}{\overset{-\mathrm{L}}{\rightleftharpoons}} \underset{\mathbf{2}}{\mathrm{Pd(etac\text{-}}O,O')_2} \qquad (1)$$

turns to **4a** in about 3 h, and **3b** to **4b** in 30 min almost completely, whereas **3d** attains equilibrium rapidly, the quotient $Q = [\mathbf{4}]/[\mathbf{3}]$ being 0.6 at 25 °C. These observations are reconciled with the molecular weight data in Table I. The value of Q diminishes with increasing basicity of L: 2-Mepy $\gg$ $PhCH_2NH_2$ > n-$BuNH_2$.

In the case of acetylacetonate complexes the carbon-bonded state is much less favorable than in ethyl acetoacetate complexes. Thus Pd(acac-O,O')(acac-C^3)py is transformed to Pd(acac-O,O')$_2$ in chloroform at room temperature almost completely in several days. Furthermore Pd(acac-C^3)$_2$(py)$_2$ cannot be identified even when Pd(acac-O,O')$_2$ is dissolved in pyridine. (See eq 2.) The trend of acetylacetone to favor the

$$\mathrm{Pd(acac\text{-}}C^3)_2\mathrm{L}_2 \overset{+\mathrm{L}}{\rightleftharpoons} \mathrm{Pd(acac\text{-}}O,O')(\mathrm{acac\text{-}}C^3)\mathrm{L} \underset{+\mathrm{L}}{\overset{-\mathrm{L}}{\rightleftarrows}} \mathrm{Pd(acac\text{-}}O,O')_2 \qquad (2)$$

O,O'-chelation in contrast to the reverse trend of ethyl acetoacetate is parallel with the enol-favoring character in the keto–enol tautomerism. Similar studies on the other β-diketone complexes are now in progress in order to elucidate the factors influencing their bonding modes.

Registry No. **1**, 62415-50-3; *cis*-Pd(etac-O,O')$_2$, 62447-40-9; *trans*-Pd(etac-O,O')$_2$, 62447-41-0; *cis*-Pd(etac-C^2)$_2$(py)$_2$, 62447-42-1; *trans*-Pd(etac-C^2)(py)$_2$, 62447-43-2; *cis*-Pd(etac-C^2)$_2$(2-Mepy)$_2$, 62504-19-2; *trans*-Pd(etac-C^2)$_2$(2-Mepy)$_2$, 58658-82-5; **3d**, 62447-44-3; **3e**, 58658-83-6; **3f**, 58658-85-8; *cis*-Pd(etac-O,O')(etac-C^2)(2,6-Me$_2$py), 62415-51-4; *trans*-Pd(etac-O,O')(etac-C^2)(2,6-Me$_2$py), 62447-45-4; **4d**, 62415-52-5; Pd(acac-O,O')(acac-C^3)(2-Mepy), 62415-41-2; Pd(acac-O,O')(acac-C^3)(3-Mepy), 62415-42-3; Pd(acac-O,O')(acac-C^3)(4-Mepy), 62415-43-4; Pd(acac-O,O')(acac-C^3)(3,5-Me$_2$py), 62460-43-9; *cis*-Pd(etac-O,O')(etac-C^2)(py), 62504-64-7; *trans*-Pd(etac-O,O')(etac-C^2)(py), 62415-44-5; *cis*-Pd(etac-O,O')(etac-C^2)(2-Mepy), 62415-45-6; *trans*-Pd(etac-O,O')(etac-C^2)(2-Mepy), 62447-35-2; *cis*-Pd(etac-O,O')(etac-C^2)(3-Mepy), 62415-46-7; *trans*-Pd(etac-O,O')(etac-C^2)(3-Mepy), 62447-36-3; *cis*-Pd(etac-O,O')(etac-C^2)(4-Mepy), 62415-47-8; *trans*-Pd(etac-O,O')(etac-C^2)(4-Mepy), 62447-37-4; *cis*-Pd(etac-O,O')(etac-C^2)(2,5-Me$_2$py), 62415-48-9; *trans*-Pd(etac-O,O')(etac-C^2)(2,5-Me$_2$py), 62447-38-5; *cis*-Pd(etac-O,O')(etac-C^2)(PPh$_3$), 62447-39-6; *trans*-Pd(etac-O,O')(etac-C^2)(PPh$_3$), 62415-29-6; Pd(acac-O,O')(acac-C^3)(py), 34710-55-9; Na_2PdCl_4, 13820-53-6.

References and Notes

(1) (a) Wakayama University. (b) Osaka City University.
(2) Ligand abbreviations and numbering: acacH = acetylacetone, $C^1H_3C^2OC^3H_2C^4OC^5H_3$; etacH = ethyl acetoacetate, $C_2H_5OC^1OC^2H_2C^3OC^4H_3$.
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