  Bull. Chem. Soc. Jpn., 56, 1393—1400 (1983)

Mixed-ligand Palladium(II) Complexes Containing *O,O'*-Chelated β-Diketonate and η^3-Carbon-bonded Ethyl 3-Oxobutanoate Anions. Preparation and Reactions with Some Lewis Bases**

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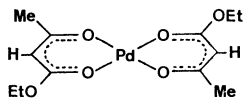
(Received October 20, 1982)

Novel palladium(II) complexes [Pd(β-dik)(η^3-etac)] (**5**), in which anions of a β-diketone and ethyl 3-oxobutanoate coordinate to the central metal atom by the *O,O'*-chelation and the η^3 carbon bonding, respectively, were prepared by the reactions of a dinuclear complex [PdCl(η^3-etac)]$_2$ with thallium(I) β-diketonates in benzene or acetone at room temperature. Reactions of **5** with Lewis bases (L) such as triphenylphosphine, diethylamine, propylamine and benzylamine were investigated. In almost all reactions, only the η^3-carbon-bonded ester ligand in **5** was converted into a terminal-carbon-bonded one to afford complexes [Pd(β-dik)(etac-C^4)L]. The bonding modes for the ligands in these products as well as in **5** were determined by means of IR and ^{1}H and ^{13}C NMR spectroscopy.

Four kinds of coordination modes for the monoanion of ethyl 3-oxobutanoate have been observed so far in palladium(II) complexes: *O,O'*-chelation (**1**, **3**),[1] η^3 carbon bonding (**2**),[2] central carbon bonding (**3**),[1] and terminal carbon bonding (**4**).[3]



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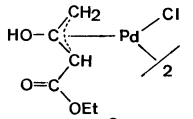

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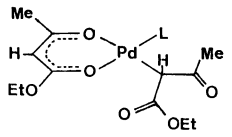

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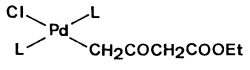
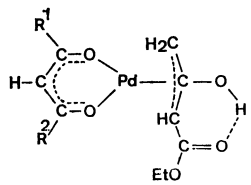


4

Of these complexes, **3** and **4** were derived from **1** and **2** by the reactions with Lewis bases, respectively.

Similarly, all these bonding modes described above[4–6] as well as *O*-unidentate bonding[7,8a,b] have also been established for 2,4-pentanedione and other β-diketones in palladium(II) and platinum(II) complexes. Comprehensive studies on the interconversion among these bonding modes of β-diketonate anions have recently been performed.[8]

As the continuation of this line of studies, we intended to prepare novel complexes of palladium(II) which involve two kinds of coordination modes for β-diketonate monoanions and to examine relative stability of each bonding mode. In this paper, preparation and characterization of complexes **5a**—**c** and their reactions with some Lewis bases to show which bonding mode is less stable are described.



	R^1	R^2
5a	CH_3	CH_3
5b	$CH_3(CF_3)$	$CF_3(CH_3)$
5c	CF_3	CF_3

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Results and Discussion

Preparation and Characterization of Complexes **5**. The η^3 complex of ethyl 3-oxobutanoate anion with palladium(II), [PdCl(η^3-etac)]$_2$ (**2**), which was first prepared by Tezuka *et al.*,[2a] was used as a starting material for preparation of complexes **5**. The bridge-splitting and concurrent chloride-abstracting reactions of **2** with twice molar amounts of thallium(I) β-diketonates yielded mononuclear complexes **5a**, **5b**, and **5c** in high yields, whose analytical data are given in Table 1.

The ^{1}H NMR data for complexes **5** in $CDCl_3$ are listed in Table 2 and compared with those for **2** which were previously reported[9] and reasonably interpreted on the basis of the η^3 structure confirmed by X-ray analysis.[2b] Complex **5c** shows five signals due to the etac ligand, together with a singlet at 6.12 ppm attributable to the methine proton of the *O,O'*-chelated hfac ligand.[4] These five signals from etac appear as a singlet at 3.74 ppm, two doublets at 2.80 and 3.87 ppm, a triplet at 1.36 ppm and a multiplet centered at 4.3 ppm, with relative intensities of 1:1:1:3:2. The first three signals can be assigned to the H^a, H^b, and H^c protons of the allylic moiety and the others to methyl and methylene protons of the ethyl groups by comparison with those of **2**. The spectral pattern similar to that of the starting complex **2** confirms that the η^3 structure of the etac ligand in **2** is maintained intact in the reaction product **5c**, although the H^d signal observed for **2** can not be detected for **5c**. This conclusion is firmly supported by the ^{13}C NMR for **5c** and **2** listed in Table 3. Both spectral data are in fairly good agreement with each other, although three additional signals from hfac appear in the spectrum of **5c**. The three signals resonate at 90.1, 175.4, and 117.8 ppm from internal Me_4Si and each couples to ^{19}F nuclei appearing as a multiplet, a quartet and a quartet, respectively, the coupling constants increasing in this order. These signal frequencies and

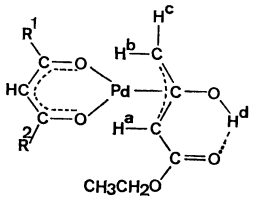
** In this paper β-dik represents a monoanion of β-diketones such as 2,4-pentanedione (acacH), 1,1,1-trifluoro-2,4-pentanedione (tfacH), and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfacH), etac denoting that of ethyl 3-oxobutanoate.

TABLE 1. ANALYTICAL DATA FOR THE NEWLY PREPARED COMPLEXES

No.	Complex	Found(Calcd)(%) C	H	N	Mol wt[a)]
5a	[Pd(acac)(η^3-etac)]	39.56(39.48)	4.68(4.81)		
5b	[Pd(tfac)(η^3-etac)]	33.65(33.97)	3.33(3.37)		
5c	[Pd(hfac)(η^3-etac)]	29.66(29.85)	2.28(2.28)		
6a	[Pd(acac)(etac-C^4)(PPh_3)]	57.68(58.35)	5.24(5.23)		596(597)
6b	[Pd(tfac)(etac-C^4)(PPh_3)]	53.69(53.61)	4.25(4.34)		654(651)
6c	[Pd(hfac)(etac-C^4)(PPh_3)]	50.63(49.42)	3.61(3.58)		715(705)
6d	[Pd(acac)(etac-C^4)(Et_2NH)]	43.96(44.18)	6.56(6.67)	3.36(3.43)	402(418)
6e	[Pd(tfac)(etac-C^4)(*n*-$PrNH_2$)]	38.21(37.56)	5.04(4.95)	3.24(3.13)	477(478)
7	[Pd(etac-C^4)($PhCH_2NH_2$)$_3$](hfac)	50.31(50.31)	4.87(4.88)	5.54(5.50)	

a) In CH_2Cl_2 at 28 °C.

TABLE 2. ^{1}H NMR DATA FOR COMPLEXES **5** IN $CDCl_3$[a)]



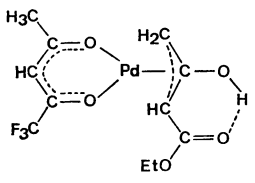
5

Complex	R^1	R^2	β-dik CH_3	CH	η^3-etac[b)] CH_3-CH_2	H^c	H^b	H^a	H^d	Coupling constants in Hz
2					1.31 t	4.29m	3.74 d	2.59 dd	3.59	10.46 d J(bc)=3.4, J(bd)=1.2, J(CH_3-CH_2)=7.2
5a	CH_3	CH_3	1.94, 1.98	5.35	1.37 t	4.3m	3.58 d	2.58 d	3.48	J(bc)=4.0, J(CH_3-CH_2)=8.0
5b	CH_3	CF_3	2.09, 2.12	5.73	1.36 t, 1.38 t	4.3m	3.69 d	2.68 d	3.59	J(bc)=3.0, J(CH_3-CH_2)=6.8
5c	CF_3	CF_3		6.12	1.36 t	4.3m	3.87 d	2.80 d	3.74	J(bc)=4.0, J(CH_3-CH_2)=8.0

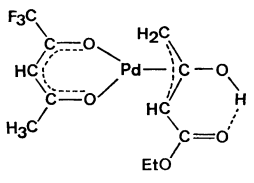
a) Chemical shifts in ppm from internal Me_4Si at 33 °C. d: Doublet, dd: doublet of doublets, t: triplet, m: multiplet. b) H^d proton signals for **5** are not observable.

coupling constants are compatible with those for the *O*,*O*′-chelate of hfac.[4)]

As is seen in Table 2, the similarity of the ^{1}H NMR data for **5b** to those for **5c**, except the additional methyl signal from tfac in **5b**, shows that the coordination structures of the β-dik and etac ligands around palladium are the same in these complexes. Owing to the unsymmetrical nature of tfac, two geometrical isomers, *cis*(CH_3,CH_2) and *trans*(CH_3,CH_2), coexist in the case of **5b**.



cis(CH_3,CH_2)

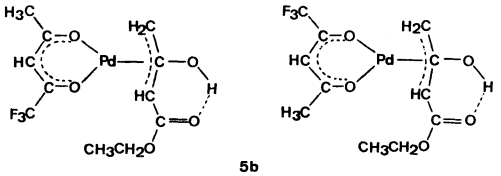


trans(CH_3CH_2)

Although the very slight splitting is recognized in the methyl signals from the tfac and ester ligands, other signals do not discriminate these two isomers. On the other hand, the ^{13}C NMR spectrum (Table 3) of **5b** clearly exhibits the presence of *cis*(CH_3,CH_2) and *trans*(CH_3,CH_2) isomers in $CDCl_3$, two sets of signals attributable to the trifluoromethyl-substituted carbonyl carbon and the methyl and methylene carbons of ethyl group appearing at 167.8, 14.0, 62.0 and at 168.3, 14.5, 62.2 ppm, respectively. Each set of signals can be assigned only arbitrarily to the cis or trans isomer.

Complexes **5** including the acac complex **5a** are soluble in most organic solvents such as haloalkanes, ketones, ethers, aromatic hydrocarbons, and even in hexane. Although **5b** and **5c** are stable in these organic solvents, **5a** is rather unstable and a less soluble substance precipitates from its solution in chloroform on addition of hexane, which is not isolated in a pure form (see Experimental section). The ^{1}H NMR spectrum of **5a** in $CDCl_3$, therefore, includes some signals other than those assignable to [Pd(acac)-(η^3-etac)], even immediately after dissolution. Only the latter signals are listed in Table 2. In this case, two methyl signals from acac are observed at 1.94 and 1.98 ppm and such different environments of the

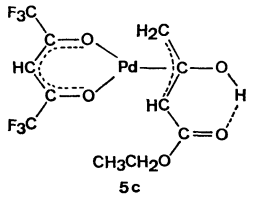
TABLE 3. ^{13}C NMR DATA FOR COMPLEXES **5b** AND **5c** IN $CDCl_3$[a)]



5b

cis(CH_3,CH_2) *trans*(CH_3,CH_2)

tfac					η³-etac			
CH_3	CH	CF_3	$CF_3\underline{C}O$	$CH_3\underline{C}O$	CH_3-CH_2	CH_2	CH	C-OH
28.8	95.2	118.8 q (285)	167.8 q, 168.3 q (33)	194.5	14.0, 14.5 / 62.0, 62.2	41.2	42.1	154.8



5c

	hfac			η³-etac					
	CH	CF_3	$CF_3\underline{C}O$	CH_3-CH_2		CH_2	CH	C-OH	C=O
2				14.5	62.3	46.4	47.7	152.0	175.4
5c	90.1 m (2)	117.8 q (285)	175.4 q (34)	13.9	62.5	42.4	43.2	156.0	175.7

a) Chemical shifts in ppm from internal Me_4Si. Figures in parentheses give $J(^{19}F$-C) in Hz. q: Quartet, m: multiplet.

TABLE 4. CHARACTERISTIC IR BANDS IN NUJOL[a)]

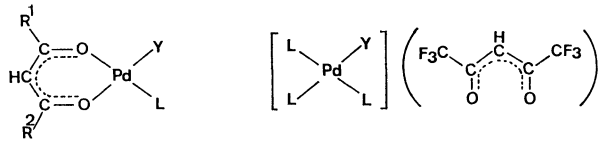
Complex	β-dik	etac			
	$\nu(C{=}O)+\nu(C{=}C)$ / cm^{-1}	$\nu(OH)/cm^{-1}$	$\nu(C{=}O)/cm^{-1}$ Ester	Ketone	δ(CCC) or ν(Pd-C)/cm^{-1}
2[b)]		3200 m	1675 vs		548 s
5a	1577 vs, 1520 vs	3200 w	1673 s		548 w
5b	1610 vs, 1523 m	3200 w	1670 s		545 w
5c	1627 vs, 1605 s, 1557 m, 1532 m	3200 w	1675 s		543 w
6a	1580 vs, 1515 vs		1743 s	1661 s	c)
6b	1620 vs, 1520 m		1741 s,	1665 s	c)
6c	1625 vs, 1540 m		1745 vs	1670 s	c)
6d	1568 vs, 1525 vs		1745 vs	1640 s	540 m
6e	1615 vs, 1517 m		1725 vs	1630 s, sh	d)
7	1661 vs		1698 s	1645 vs	525 s

a) vs: Very strong, s: strong, m: medum, w: weak, sh: shoulder. b) Ref. 3a. c) Not assignable due to overlapping with the ligand bands of triphenylphosphine. d) Not detectable.

methyl hydrogens are caused by unsymmetric coordination of the ester ligand in **5a**.

Table 4 lists the characteristic IR bands of complexes **5** and products of their reactions with Lewis bases. The bonding modes of the β-dik and etac ligands are easily diagnosed on the basis of the spectral pattern in the 1500—1700-cm^{-1} region. Two or four bands observed in the 1520—1627-cm^{-1} region for **5** are assigned to the $\nu(C{=}O)+\nu(C{=}C)$ vibrations of the *O,O'*-chelates of β-dik,[4)] while a band in the 1670—1675-cm^{-1} region is assigned to the $\nu(C{=}O)$(ester) of the η^3-carbon-bonded etac ligand.[2a)] Weak bands around 545 and 3200 cm^{-1} are attributed to the δ(CCC) and ν(OH) vibrations, respectively, characteristic of the η^3 carbon bonding of etac by reference to the data for complex **2**.[2a)]

TABLE 5. ^{1}H NMR DATA FOR COMPLEXES **6** AND **7** IN $CDCl_3$[a]



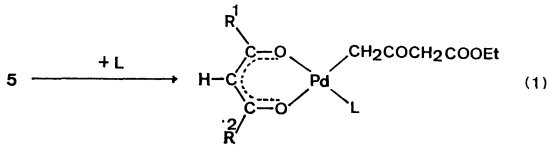
6 **7**

(Pd-Y = Pd-$CH_2COCH_2COOCH_2CH_3$)

Complex	R^1	R^2	L	β-dik		etac-C^4			
				CH_3	CH	CH_3-CH_2		CH_2	CH_2-Pd
6a	CH_3	CH_3	PPh_3	1.58, 2.00	5.27	1.19 t	4.09 q	3.54	2.26 d {4}
6b[b] *cis*(CH_3,P)	CH_3	CF_3	PPh_3	1.74	5.72	1.18 t	4.12 q	3.56	2.31 d {3}
6b[b] *trans*(CH_3,P)	CF_3	CH_3	PPh_3	2.18				3.62	2.40 d {3}
6c	CF_3	CF_3	PPh_3		6.30	1.23 t	4.26 q	3.64	2.59 d {2}
6d[c]	CH_3	CH_3	Et_2NH	1.90	5.27	1.27 t	4.19 q	3.56	2.67
6e[c]	CH_3, CF_3		*n*-$PrNH_2$	2.10	5.71	1.30 t	4.22 q	3.55	2.72
					5.73				2.76
7[c]	CF_3	CF_3	$PhCH_2NH_2$		5.62	1.22 t	4.15 q	3.64	2.30

a) Same as footnote a) for Table 2. Figures in braces give $^3J(^{31}P\text{-}H)$ in Hz. b) Data for the low-temperature limitting spectrum at −29 °C are given. c) Chemical shifts for L. Et: 2.7 m, 1.42 t (for **6d**). *n*-Pr: 2.7 m, 1.7 m, 0.99 t (for **6e**). CH_2: 3.49 (for **7**).

Reactions of **5** *with Lewis Bases Producing Terminal-carbon-bonded Complexes of etac.* Although the reactions of complexes **5** with triphenylphosphine and a variety of nitrogen bases such as propylamine, diethylamine, *t*-butylamine, benzylamine, pyridine, and piperidine were tried, only five complexes of the type **6** and complex **7** listed in Table 1 could be isolated as reaction products in pure forms. Quite high solubilities of these products in most organic solvents described earlier make those isolation difficult. When complexes **5** were allowed to react with an equimolar amount of triphenylphosphine in benzene or chloroform, the η^3 carbon bonding of the etac ligand in **5** was converted into the terminal carbon bonding to afford neutral complexes **6a**, **6b**, and **6c**.



(1)

	R^1	R^2	L
6a	CH_3	CH_3	PPh_3
6b	CH_3(CF_3)	CF_3(CH_3)	PPh_3
6c	CF_3	CF_3	PPh_3
6d	CH_3	CH_3	Et_2NH
6e	CH_3(CF_3)	CF_3(CH_3)	*n*-$PrNH_2$

Similarly, diethylamine and propylamine reacted with **5a** and **5b** to produce **6d** and **6e**, respectively. In contrast with these bases, benzylamine reacted with **5c** to give solely the cationic complex **7**, irrespective of the reactant mole ratio, which has hfac as a counter anion in the outer sphere.

$$\mathbf{5c} \xrightarrow{+3L} [Pd(CH_2COCH_2COOEt)L_3](CF_3COCHCOCF_3) \quad \mathbf{7}\ (L=PhCH_2NH_2) \qquad (2)$$

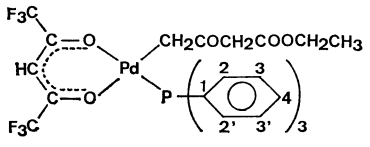
The analytical and molecular weight data for these complexes isolated are also included in Table 1.

The ^{1}H NMR data for complexes **6** and **7** are collected in Table 5. The H^a, H^b, and H^c signals observed for **5** are lost in **6a**—**c** and instead two signals appeared at 3.54—3.64 and 2.26—2.59 ppm as a singlet and a doublet with relative intensity of 1:1, each signal corresponding to 2H protons. Such a spectral change indicates that the η^3-carbon-bonded etac ligand in **5** was converted into the terminal-carbon-bonded one in **6a**—**c** as shown by Eq. 1. Thus, the singlet and the doublet are assigned to protons of the central methylene and the terminal methylene coordinated to palladium, respectively, by reference to the spectral data of **4** (L=py or 1/2·bipy).[3a] The latter methylene protons couple to ^{31}P cis to them to give a doublet with $^3J(P\text{-}H) = 2\text{—}4$ Hz.

As Fig. 1a shows, the ^{1}H NMR spectrum of **6a** in the methyl and methylene proton regions exhibits two methyl signals from acac at 1.58 and 2.00 ppm. The lower-field signal is assigned to the methyl protons trans to P, while the higher-field one to the methyl cis to P because such an appreciable upfield shift is caused by the anisotropic shielding effect of triphenylphosphine at the cis position.[6a]

Figure 1b shows the variable-temperature ^{1}H NMR spectra of **6b** in the same regions as in Fig. 1a. The spectrum at room temperature (33 °C) is composed of a broad singlet (3.56 ppm), a broad doublet (2.37 ppm), and two collapsed signals (*ca.* 1.7 and 2.2 ppm). With increasing temperature, the first two signals sharpen, while the other two give a coalesced signal. On the other hand, as the temperature is lowered, the first two signals become broader and split, and then sharpen to give two sets of signals each composed of a singlet and a doublet at −29 °C. Similarly, other two signals gradually sharpen with decreasing temperature finally giving two sharp singlets at 1.74 and 2.18 ppm, which correspond to resonances of the meth-

TABLE 6. ^{13}C NMR DATA FOR COMPLEX **6c** IN $CDCl_3$[a)]



6c

hfac				etac-C^4				
CH	CF_3	$CF_3\underline{C}O$	CH_3-CH_2		CH_2-Pd	CH_2	C=O(O)	C=O
89.9	117.4q, 117.7q (285) (285)	174.9q (35)	14.1	60.7	26.9d [5.1]	50.4	168.3	205.6

a) Same as footnote for Table 3. Figures in parentheses and brackets give $J(^{19}F\text{-}C)$ and $J(^{31}P\text{-}C)$, respectively. Chemical shifts for PPh_3: C^1, 127.6 d[55.7]; C^2, 134.4 d[11.1]; C^3, 128.6 d[11.1]; C^4, 131.3 d[2.6].

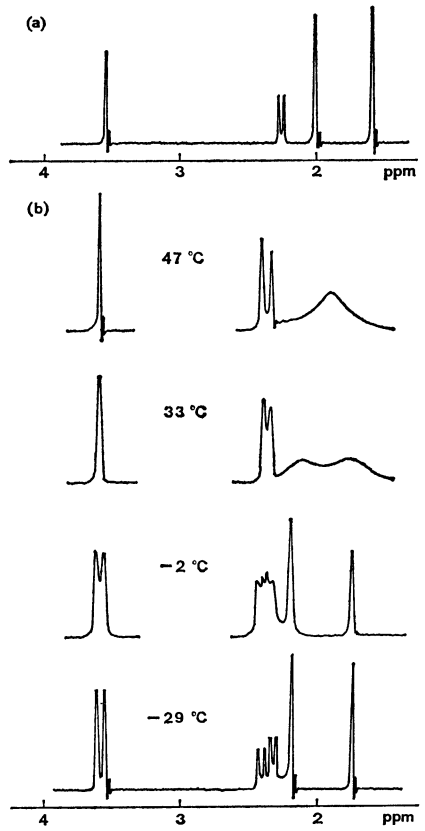
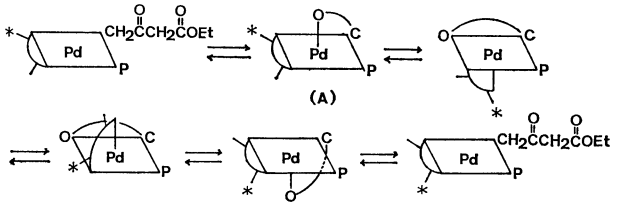


Fig. 1. ^1H NMR spectra at 100 MHz of (a) [Pd(acac)(etac-C^4)(PPh_3)], **6a** ($CDCl_3$; 33 °C) and (b) [Pd(tfac)(etac-C^4)(PPh_3)], **6b** ($CDCl_3$; −29, −2, 33, and 47 °C) in the methyl and methylene proton regions.

yl groups cis and trans to P (compare Figs. 1a and 1b). These results imply that complex **6b** exists as a mixture of two geometrical isomers, *cis*(CH_3, P) and *trans*(CH_3, P) (in the mole ratio of 1:1.3), in $CDCl_3$ at −29 °C and these isomers are readily interconvertible at 33 °C and above. In Table 5, the low-temperature limitting spectral data for these isomers are given.

Table 6 denotes the ^{13}C NMR data for **6c** as a representative of **6** which gives the most simple spectrum. Two trifluoromethyl signals appear at 117.4 and 117.7 ppm as quartets with $^1J(C\text{-}F)=285$ Hz, thus reflecting the slight difference in environments caused by the trans ligands, etac and triphenylphosphine and also showing stereochemical rigidity of this complex in $CDCl_3$ at room temperature.

Much attention has recently been given to the mechanisms of geometrical isomerization of the square-planar metal complexes.[10] In the case of the present complex **6b**, coupling of the terminal methylene protons of etac to ^{31}P is maintained during the isomerization (see Fig. 1b), showing inapplicability of the dissociative mechanism involving the Pd–P bond rupture. Thus the transformation, as depicted below, of a five-coordinate intermediate **A**, in which the fifth coordination site of palladium is occupied by the ester carbonyl oxygen atom, may be the most probable mechanism to be proposed:



The *C,O*-chelation of tfac as in **A** has been found as a stable bonding mode for the tfac dianion in a series of [Pd(tfac(2-)-*C,O*)LL']-type complexes[11] and the Pt(II) analogues.[12] An intermolecularly associated complex, in which the metal atom of a reacting species is coordinated by the ester carbonyl oxygen of a neighboring molecule, is also conceivable as an alternative intermediate for the coordination-site exchange. Such an example that another molecule of the same species acts as a catalyst was found for the σ-pyridyl complex, [Pd(acac)(σ-pyridyl)PPh_3], and the effect was termed "self catalysis" by Tanaka *et al.*[13] Similar phenomenon was also observed for [Pd(acac)(CH_2CN)PPh_3].[14] As described above, complexes **6a** and **6c** are stereochemically rigid in $CDCl_3$ at room temperature, while **6b** shows fluxional motion under the same conditions. However, it is not rationalized why only complex **6b** having the unsymmetric tfac ligand brings about the coordination-site exchange.

As is seen in Table 5, reaction products with nitrogen bases, both **6d** and **6e**, show only a single methyl

signal from β-dik in their ^{1}H NMR spectra. Two possibilities are conceivable: 1) Accidental coincidence of the two methyl signals; 2) coalescence to a single peak by coordination-site exchange of the β-dik ligand. In the present case, the second possibility to occur will probably be excluded because the acac complex **6a** does not cause such a reaction and **6e** shows two methine and CH_2–Pd proton signals corresponding to the *cis*(CH_3,N) and *trans*(CH_3,N) isomers.

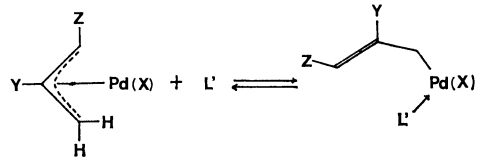
The product complex, **7**, from the reaction of **5c** with benzylamine gave satisfactory analysis as Pd(etac)(hfac)$(PhCH_2NH_2)_3$ which differs from other products, **6**, in composition. However, the coordination mode of etac to palladium is the same as that in **6** on the basis of the similarity of ^{1}H NMR data (Table 5). On the other hand, the methine proton from hfac in **7** resonates at higher field (5.62 ppm) than that (6.30 ppm) in **6c**. Such an upfield shift of the methine proton signal is generally observed for the outer-sphere complexes of the type $[PdL_4](hfac)_2$ compared with the *O,O'*-chelate because of the higher charge density on noncoordinating anion: the methine protons of $[Pd(hfac)_2]$,[4] $[Pd(n\text{-}PrNH_2)_4](hfac)_2$,[8a] $[Pd(py)_4](hfac)_2$,[8b] and $[Pd(PMe_2Ph)_4](hfac)_2$[8b] resonate at 6.42, 5.92, 6.00, and 5.67 ppm in $CDCl_3$, respectively.

When the IR spectral data (Table 4) of **5** and **6** are compared with each other, a considerable difference is noticed only in the absorption bands characteristic of the etac ligand. Thus complexes **5** have the ν(OH) and ν(C=O)(ester) bands at around 3200 and 1670 cm^{-1}, respectively, while complexes **6** show no absorption bands around 3200 cm^{-1}, but exhibits two strong ν(C=O) vibrations in the 1725—1745 and 1630—1670-cm^{-1} regions. This confirms the above-mentioned conclusion that the η^3-carbon-bonded enolate anion of 3-oxobutanoate was converted into the terminal-carbon-bonding of the keto tautomer. These carbonyl bands assignable to the ν(C=O)(ester) and ν(C=O)(keto) vibrations are also found for complexes of the type **4** as follows: [PdCl(etac-*C*^{4})$(py)_2$] 1740vs, 1650vs; [PdCl(etac-*C*^{4})(bipy)] 1730vs, 1640vs.[3a]

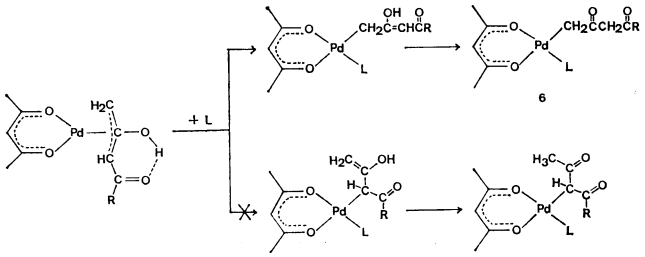
The IR spectrum of complex **7** has four bands of strong to medium intensities in the 1600—1700-cm^{-1} region. Of these, a medium band observed at 1619 cm^{-1} is assigned to the δ(NH_2) vibration of the coordinated benzylamine and hence omitted in Table 4. Although two strong bands at 1698 and 1645 cm^{-1} are slightly closer mutually than those for **6**, they can be assigned to the ν(C=O) vibrations of the terminal-carbon-bonded etac ligand. On the other hand, no band shows in the region attributable to the ν(C=O) + ν(C=C) vibrations of the *O,O'*-chelated β-dik ligand, but instead a strong band appears at 1661 cm^{-1}. The frequency of this band is close to that for potassium 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate, thus conforming to the cationic formulation [Pd(etac-*C*^{4})$(PhCH_2NH_2)_3$](hfac) which was deduced from the ^{1}H NMR spectral data.

Consideration on Bonding Nature of the β-dik and etac Ligands in ***5***. As described before, complexes **5b** and **5c** are stable in solution, but **5a** is rather unstable in most organic solvents and decomposes to give an uncharacterized crude substance. The stability difference among these complexes may be brought about by the substituent effect for the methyl groups of acac. The more basic acac ligand can coordinate more tightly to palladium than tfac and hfac do and destabilize the η^3-carbon-bonding of etac to the metal as a result. The conversion of the η^3-carbon-bonded etac ligand in **5a** into the terminal-carbon-bonded one without any free ligand in solution could produce a less soluble substance in which presumably the vacant site of palladium is coordinated by a free carbonyl oxygen of another molecule.

In all the reactions of **5** with Lewis bases except that of **5c** with benzylamine, it was found that the O,O'-chelate of the β-dik ligand in **5** is more stable than the η^3 carbon bonding of etac and the latter was converted into the terminal-carbon-bonding. Powell *et al.* have studied insertion reactions of olefins,[15] 1,2-dienes,[16] and 1,3-dienes[17] (L') into the allylic palladium bonds of the η^3-allylic complexes (η^3-allyl)Pd(X) (X=hfac, acac, or chloride). In either case of the bidentate ligands (hfac and acac), the η^1-allylic complex (η^1-allyl)(L')Pd(X) was conceivable as



an intermediate on the basis of *syn-anti* proton exchange on the NMR time scale, whereupon the less substituted terminal carbon of the allylic moiety invariably linked with the metal atom. These results are also in accord with the present case to give **6** but not the central-carbon-bonded etac complexes as follows:



However, similar palladium(II) complexes, **3**, containing the central-carbon-bonded etac ligand have been prepared so far by the reactions of bis-*O,O'*-chelate, **1**, with L (L=a variety of nitrogen bases).[1]

Experimental

Preparation of Complexes ***5***. The starting dinuclear η^3 complex, $[PdCl(\eta^3\text{-etac})]_2$ (**2**) was prepared according to the Yanase's modification[9] of the method originally proposed by Tezuka.[2a]

[Pd(acac)(η^3-etac)] ***(5a)***: Complex **2** (225 mg, 0.415 mmol) was dissolved in benzene (30 cm^3) on heating and then the solution was cooled to room temperature. Thallium(I) 2,4-pentanedionate (277 mg, 0.913 mmol) was added to the solution and the mixture was stirred for 2 h at room temperature. After standing for further 2—3 h, the mixture was filtered to remove thallium(I) chloride precipitated

and the filtrate was concentrated to 5 cm³ under reduced pressure. On addition of hexane, a crude decomposition product was deposited and again removed by filtration. The filtrate was evaporated to dryness to obtain a yellow solid (214 mg) in a 71% yield.

The crude substance shows no IR band at 3200 cm^{-1}, which is assigned to the ν(OH) vibration of the η^3-carbon-bonded etac, but instead shows a new strong IR absorption at 1620 cm^{-1}. The substance has not been further characterized because of its poor solubility in most organic solvents.

*[Pd(tfac)(η³-etac)] (**5b**)*: Thallium(I) 1,1,1-trifluoro-2,4-pentanedionate (326 mg, 0.913 mmol) was added to a suspension of **2** (225 mg, 0.415 mmol) in acetone (20 cm³). After being stirred for 30 min at room temperature, the mixture was allowed to stand for further 2—3 h to precipitate thallium(I) chloride, which was filtered and the filtrate was then concentrated to 2—3 cm³ under reduced pressure. On addition of hexane to the concentrate, a pale yellow solid (246 mg) was obtained in a 76% yield.

*[Pd(hfac)(η³-etac)] (**5c**)*: To a suspension of **2** (225 mg, 0.415 mmol) in acetone (20 cm³) was added thallium(I) 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate (376 mg, 0.913 mmol). After being stirred for 30 min at room temperature, the mixture was allowed to stand for additional 2—3 h and then filtered to give a transparent solution, which was evaporated to dryness under reduced pressure. The residue was redissolved in hexane and filtered again to remove a small amount of insoluble substance. The filtrate was evaporated to dryness under reduced pressure, affording a pale yellow solid (302 mg) in an 82% yield.

*Reactions of [Pd(β-dik)(η³-etac)] (**5**) with Lewis Bases. **5a** with Triphenylphosphine*: Triphenylphosphine (156 mg, 0.598 mmol) was added to a benzene (15 cm³) solution of **5a** (200 mg, 0.598 mmol) and the mixture was stirred for 20 min at room temperature. The solvent was then evaporated to 2—3 cm³ under reduced pressure before adding hexane to deposit a yellow powder of [Pd(acac)(etac-C^4)(PPh_3)] (**6a**). Scratching the flask was necessary to deposit **6a** effectively. Recrystallization from benzene–hexane gave a yellow crystalline solid (303 mg) in an 85% yield.

***5b** with Triphenylphosphine*: Complex **5b** (100 mg, 0.257 mmol) was also allowed to react with triphenylphosphine (68 mg, 0.26 mmol) in benzene (10 cm³) at room temperature. After being stirred for 30 min, the solution was concentrated to 2—3 cm³ under reduced pressure and hexane was added to the concentrate. A yellow crystalline solid of [Pd(tfac)(etac-C^4)(PPh_3)] (**6b**), deposited from the solution on standing at room temperature. The yield was 139 mg (81%).

***5c** with Triphenylphosphine*: Chloroform (10 cm³) was used as a solvent for the reaction of **5c** (100 mg, 0.226 mmol) with triphenylphosphine (59 mg, 0.23 mmol). When the reaction mixture was stirred for 20 min at room temperature and then concentrated under reduced pressure, an oily substance was obtained, which was extracted with petroleum ether and the extract was left at −20 °C to give an orange crystalline solid of [Pd(hfac)(etac-C^4)(PPh_3)] (**6c**). The yield was 76 mg (48%).

***5a** with Diethylamine*: Diethylamine (0.07 cm³, 0.677 mmol) was added to a benzene (15 cm³) solution of **5a** (200 mg, 0.598 mmol) and the mixture was stirred for 1 h at room temperature before the solvent was evaporated to 2—3 cm³ under reduced pressure. A pale yellow powder of [Pd(acac)(etac-C^4)(Et_2NH)] (**6d**), was deposited by scratching the flask after the addition of hexane. Recrystallization from benzene–hexane gave a crystalline solid in a 53% yield (132 mg).

***5b** with Propylamine*: Propylamine (0.03 cm³, 0.364 mmol) was added to a benzene (10 cm³) solution of **5b** (140 mg, 0.360 mmol) and the mixture was stirred for 20 min at room temperature. Evaporation of the solvent under reduced pressure left an oily residue, which was extracted with hexane. A yellow powder of [Pd(tfac)(etac-C^4)(*n*-$PrNH_2$)] (**6e**), precipitated from the extract on standing overnight at −20 °C. The yield was 103 mg (60%).

***5c** with Benzylamine*: A three times molar amount of benzylamine (0.10 cm³, 0.914 mmol) was allowed to react with **5c** (130 mg, 0.294 mg) in benzene (10 cm³) for 30 min with stirring at room temperature. Evaporation of the solvent under reduced pressure left an oily substance. The substance was redissolved in a small amount of acetone, hexane was added to the solution, and then the solution was kept for a week at −20 °C, from which a pale yellow powder of [Pd(etac-C^4)($PhCH_2NH_2$)$_3$](hfac) (**7**), was precipitated. The yield was 130 mg (59%). Even when an equimolar amount of benzylamine was used, the same complex **7** was produced in a low yield.

Measurements. Infrared spectra were obtained in Nujol mull with a JASCO DS 701G infrared spectrophotometer. NMR spectra were recorded on JNM-MH100 (in the case of ^1H) and FX60Q (for ^{13}C) instruments. Molecular weight was determined in dichloromethane at 28 °C with a vapor pressure osmometer manufactured by Knauer, West Berlin, West Germany.

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