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η^3 and η^1 Terminal-Carbon-Bonded Complexes of 2,4-Pentanedione with Palladium(II)

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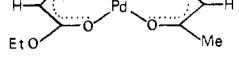
Dichlorobis(benzonitrile)palladium(II) reacts with 2,4-pentanedione (acacH) in acetone at 0 °C to afford $[PdCl(acac\text{-}O,O')]_2$ (**5**), which turns to a η^3 acac complex $[PdCl(acac\text{-}C^1\text{–}C^3)]_2$ (**6**) during a prolonged reaction at room temperature. Bridge-splitting reactions of **5** with triphenylphosphine and triphenylarsine yield $PdCl(acac\text{-}O,O')L$, where L is PPh_3 (**7a**) or $AsPh_3$ (**7b**). Corresponding mononuclear complexes $PdCl(acac\text{-}C^1\text{–}C^3)L$ (L = PPh_3 (**8a**) or $AsPh_3$ (**8b**)) and $M[PdCl_2(acac\text{-}C^1\text{–}C^3)]$ (M = PPh_4 (**9a**) or $AsPh_4$ (**9b**)) are similarly derived from **6**. The isomeric pairs **7a–8a** and **7b–8b** manifest a novel type of linkage isomerism. The reaction of **6** with 2,2′-bipyridine results in $PdCl(acac\text{-}C^1)(bpy)$, which exhibits the keto–enol tautomerism of the terminal-carbon-bonded acac, the equilibrium quotient [enol]/[keto] being 0.7 in $CDCl_3$ at 25 °C.

2,4-Pentanedione and other β-dicarbonyl compounds are very versatile ligands exhibiting various modes of bonding to metal ions.[1] In recent years four kinds of coordination modes of ethyl acetoacetate have been observed in palladium(II) complexes: O,O′ chelation (**1**, **3**),[2] η^3-allylic bonding (**2**),[3] η^1 central carbon bonding (**3**),[2] and terminal carbon bonding (**4**).[4]



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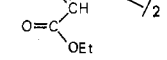

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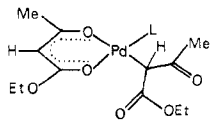

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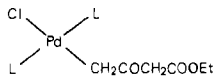

4

In order to clarify the factors which make the ligand prefer a particular bonding mode, many more comparative studies are necessary employing other β-dicarbonyl compounds and various coexisting ligands. 2,4-Pentanedione (acacH), the most representative β-dicarbonyl compound, usually coordinates to a metal ion through the two oxygen atoms forming a six-membered chelate ring.[5] The central-carbon-bonded palladium(II) complexes of acacH similar to **3** were obtained by the reactions of $Pd(acac)_2$ with Lewis bases (L) such as triphenylphosphine, pyridine, and diethylamine.[6] The present paper reports the preparation and characterization of several palladium(II) complexes of acacH exhibiting η^3 bonding a little different from the delocalized η-allylic coordination in **2** and those containing terminal σ bonding similar to that in **4**.

Experimental Section

Di-μ-chloro-bis(2,4-pentanedionato)dipalladium(II), $[PdCl(acac\text{-}O,O')]_2$ (5). Dichlorobis(benzonitrile)palladium(II) (1 g, 2.6 mmol) prepared by the method of Kharasch et al.[7] was dissolved in 25 mL of a mixture (1:1 by volume) of acetone and acacH. The solution was stirred in an ice bath for 1–2 h to separate out a brown fuzzy precipitate in 22% yield, which was filtered, washed with acetone, and dried in vacuo. The compound is sparingly soluble in the usual solvents. Anal. Calcd for $[PdCl(C_5H_7O_2)]_2$: C, 24.92; H, 2.93; Cl, 14.71. Found: C, 24.50; H, 2.86; Cl, 15.25.

Di-μ-chloro-bis(η^3-1-acetyl-2-hydroxyallyl)palladium(II), $[PdCl(acac\text{-}C^1\text{–}C^3)]_2$ (6). The above-mentioned reaction between $PdCl_2(PhCN)_2$ and acacH was performed at room temperature for about 24 h. The brown precipitate once formed was gradually converted into a yellow powder, which was filtered, washed with acetone, and dried in vacuo. The yield was 40%. The compound is also sparingly soluble in usual solvents. Anal. Calcd for $[PdCl(C_5H_7O_2)]_2$: C, 24.92; H, 2.93; Cl, 14.71. Found: C, 25.37; H, 2.99; Cl, 14.88.

Chloro(2,4-pentanedionato)(triphenylphosphine)palladium(II), $PdCl(acac\text{-}O,O')PPh_3$ (7a). A benzene solution (8 mL) containing triphenylphosphine in amounts (0.1821 g) equimolar with palladium was added drop by drop with stirring to a suspension of complex **5** (0.1682 g) in benzene (3 mL). The mixture turned to a clear solution upon reaction. After filtration the solution was concentrated to ca. 5 mL by vacuum evaporation at room temperature. Ethyl ether was added to the solution to precipitate a yellow powder, which was filtered and washed with ether. The yield was 60%. Red-orange needles were obtained by recrystallization from dichloromethane–petroleum ether. Anal. Calcd for $PdCl(C_5H_7O_2)P(C_6H_5)_3$: C, 54.89; H, 4.41; mol wt, 503. Found: C, 54.60; H, 4.76; mol wt, 532.

Chloro(2,4-pentanedionato)(triphenylarsine)palladium(II), $PdCl(acac\text{-}O,O')AsPh_3$ (7b). The bridge-splitting reaction of complex **5** with triphenylarsine in a similar fashion as above afforded red-orange needles in a 79.6% yield. Anal. Calcd for $PdCl(C_5H_7O_2)As(C_6H_5)_3$: C, 50.48; H, 4.05; Cl, 6.48; mol wt, 547. Found: C, 51.04; H, 4.11; Cl, 7.82; mol wt, 593.

Chloro(η^3-1-acetyl-2-hydroxyallyl)(triphenylphosphine)palladium(II), $PdCl(acac\text{-}C^1\text{–}C^3)PPh_3$ (8a), and Chloro(η^3-1-acetyl-2-hydroxyallyl)(triphenylarsine)palladium(II), $PdCl(acac\text{-}C^1\text{–}C^3)AsPh_3$ (8b). The bridge-splitting reactions of complex **6** with triphenylphosphine or triphenylarsine were carried out in benzene at room temperature to obtain yellow powders in 84.7 and 79.4% yields, respectively. Both of them were recrystallized from dichloromethane–petroleum ether. Anal. Calcd for $PdCl(C_5H_7O_2)P(C_6H_5)_3$: C, 54,89; H, 4.41; Cl, 7.04; P, 6.15; mol wt, 503. Found: C, 54.61; H, 4.39; Cl, 7.20; P, 5.68; mol wt, 540. Calcd for $PdCl(C_5H_7O_2)As(C_6H_5)_3$: C, 50.48; H, 4.05; Cl, 6.48; mol wt, 547. Found: C, 50.41; H, 4.03; Cl, 7.36; mol wt, 584.

Di-μ-bromo-bis(η^3-1-acetyl-2-hydroxyallyl)palladium(II), $[PdBr(acac\text{-}C^1\text{–}C^3)]_2$ (6′). Dibromobis(benzonitrile)palladium(II) was allowed to react in an acetone–acacH solution at room temperature

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for about 3 days to produce a yellow powder in 33% yield. Anal. Calcd for $[PdBr(C_5H_7O_2)]_2$: C, 21.04; H, 2.47. Found: C, 21.11; H, 2.48.

Tetraphenylphosphonium and Tetraphenylarsonium Dichloro(η^3-1-acetyl-2-hydroxyallyl)palladates(II), $[PPh_4][PdCl_2(acac\text{-}C^1\text{-}C^3)]$ (9a) and $[AsPh_4][PdCl_2(acac\text{-}C^1\text{-}C^3)]$ (9b). An acetone solution (30 mL) containing excess lithium chloride was added dropwise with stirring to a suspension of complex **6** (0.1838 g) in acetone (2 mL) to result in a clear red solution. A dichloromethane solution (20 mL) containing tetraphenylphosphonium chloride in amounts (0.3194 g) equimolar with palladium was added to the red solution. After stirring for a while the solution was evaporated to dryness at room temperature under reduced pressure. The residue was extracted with dichloromethane to separate the reaction product from lithium chloride. The extract was concentrated to about 3 mL by evaporation, to which ethyl ether was added to precipitate a reddish yellow powder in a 94% yield. Recrystallization from dichloromethane–*n*-hexane afforded red-yellow crystals. A similar procedure using tetraphenylarsonium chloride in place of tetraphenylphosphonium chloride gave red-yellow crystals in an 86% yield. Anal. Calcd for $[P(C_6H_5)_4][PdCl_2(C_5H_7O_2)]$: C, 56.56; H, 4.42; Cl, 11.52; P, 5.03; mol wt, 616. Found: C, 56.26; H, 4.41; Cl, 12.27; P, 4.66; mol wt, 577. Calcd for $[As(C_6H_5)_4][PdCl_2(C_5H_7O_2)]$: C, 52.78; H, 4.12; Cl, 10.75; mol wt, 660. Found: C, 52.31; H, 4.07; Cl, 11.38; mol wt, 643.

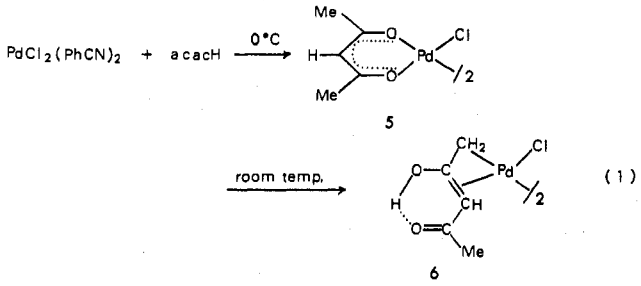
Chloro(2,4-pentanedionato-C^1)(2,2′-bipyridine)palladium(II), PdCl(acac-C^1)(bpy) (10). A chloroform solution (10 mL) containing 2,2′-bipyridine in amounts (0.0923 g) equimolar with palladium was added slowly with stirring to a suspension of complex **6** (0.1431 g) in chloroform (2 mL) to result in a clear solution. After filtration the solution was concentrated by evaporation to about 5 mL, and ethyl ether was added to the concentrate to precipitate a yellow powder in 91% yield. The product was purified by reprecipitation from chloroform–ethyl ether. Anal. Calcd for $PdCl(C_5H_7O_2)(C_{10}H_8N_2)$: C, 45.36; H, 3.81; N, 7.05; Cl, 8.93; mol wt, 397. Found: C, 45.20; H, 3.79; N, 7.14; Cl, 9.00; mol wt, 427.

Measurements. The infrared spectra of solid specimens were taken in Nujol with JASCO IR-E (4000–600 cm^{-1}) and Hitachi EPI-L (700–200 cm^{-1}) infrared spectrophotometers. IR spectra of solutions were obtained in a KIII-type cell with the JASCO IR-E instrument. The NMR spectra at room temperature were measured by means of JOEL-C-60HL and JNM-PS-100 spectrometers with tetramethylsilane as an internal reference, spectra at lower temperatures being taken with JOEL-MH-100 instrument. Molecular weight was determined in dichloromethane at 25 °C with a vapor pressure osmometer manufactured by Knauer, Berlin, Germany.

Results and Discussion

Dichlorobis(benzonitrile)palladium(II) is soluble in organic solvents and frequently used as a starting material for synthesis of various palladium(II) complexes. To the best of our knowledge, however, the reaction of $PdCl_2(PhCN)_2$ with 2,4-pentanedione has not yet been reported. We have examined this reaction with a hope that a new complex might be obtained which contains acacH as a neutral ligand in a similar fashion as was observed in several complexes of the first transition metals.[8]

The reaction between $PdCl_2(PhCN)_2$ and acacH in acetone proceeds at 0 °C to afford a brown fuzzy precipitate **5**. If the reaction is carried out at room temperature, the brown product **5** changes gradually to a yellow powder **6**. Thus compound



(1)

6 appears to be produced via **5**. The isolated compound **5** was resuspended in acetone and stirred for 24 h without any change, indicating that the transformation does not occur spontaneously. However, stirring of the suspension of **5** in acetone containing acacH for 24 h converted **5** to **6**. The free ligand plays some role in this reaction though the mechanism is not clear at present. In the course of the reaction between $PdBr_2(PhCN)_2$ and acacH to yield a yellow powder **6′**, no sign of an intermediary product corresponding to **5** was noticed. The bonding type as in **6** might be much more favorable for the bromo complex compared with the chloro complex.

Table I. Characteristic IR and Proton NMR Spectra of the O,O′-Chelated 2,4-Pentanedionato Complexes with Palladium(II)

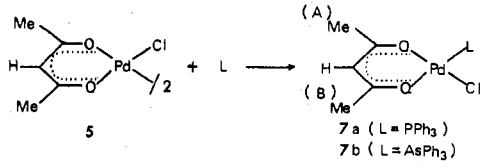
	5	7a	7b	Assignment
IR,[a] cm^{-1}	1570 vs	1568 vs	1558 vs	$\nu(C\overline{\cdots}O)$
	1555 sh	1542 sh	1541 sh	
	1519 vs	1516 vs	1516 vs	$\nu(C\overline{\cdots}C\overline{\cdots}C)$
	470 s	451 m	453 s	ν(Pd–O)
	323 vs			ν_b(Pd–Cl)
		353 m	354 m	ν_t(Pd–Cl)
NMR,[b] τ		8.46	8.38	CH_3(A)
		7.93	7.89	CH_3(B)
		4.76	4.68	CH

[a] Measured in Nujol. Key: vs, very strong; s, strong; m, medium; sh, shoulder. ν_b and ν_t stand for stretches of bridging Pd–Cl and terminal Pd–Cl, respectively. [b] Measured at 60 MHz in $CDCl_3$ with tetramethylsilane as an internal reference. The proposed structure of each compound is given in eq 2.

O,O′-Chelated 2,4-Pentanedionato Complexes. As is seen in Table I compound **5** exhibits two very strong IR bands at 1570 and 1519 cm^{-1} accompanied by a shoulder at 1555 cm^{-1} which are characteristic of the 2,4-pentanedionato chelate and assigned to the $\nu_s(C\overline{\cdots}O)$ and $\nu_{as}(C\overline{\cdots}C\overline{\cdots}C)$ vibrations.[9] A strong ν(Pd–O) band is observed at 470 cm^{-1} corresponding to that in $Pd(acac)_2$[10] at 463 cm^{-1}. A very strong band at 323 cm^{-1} which is absent in the spectrum of $Pd(acac)_2$ is ascribed to the Pd–Cl (bridging) stretching vibration. The frequency is appreciably lower than that of the Pd–Cl(terminal) stretching band observed for the mononuclear complexes **7a** and **7b** (Table I). Such a tendency has been well documented.[11]

These IR data support the binuclear structure proposed for compound **5** (eq 1) although the insolubility in common solvents prevents the determination of molecular weight and NMR spectra. Kawamoto, Imanaka, and Teranishi[12] prepared **5** by the reaction of $[PdCl_2(C_2H_4)]_2$ with acacH in refluxing dichloromethane under the stream of ethylene. The product shows satisfactory analysis and the IR bands at 1610 and 1520 cm^{-1}. In contrast to our present specimen, it was reported to be soluble in chloroform giving rise to the proton NMR signals at τ 7.75 (CH_3) and 4.42 (CH). The cause of discrepancy is not clear.

In order to solubilize compound **5**, the bridge splitting reactions (eq 2) with triphenylphosphine and triphenylarsine



(2)

were carried out in benzene at room temperature. The characteristic IR bands and NMR signals of the mononuclear complexes **7a** and **7b** are included in Table I. The proton NMR data unequivocally support the proposed structure of **7a** and **7b** (eq 2). Compound **7a** was derived via a different route in a previous paper,[6a] where the higher field signal was assigned to the methyl group (A) cis to triphenylphosphine.

The $\nu(C\overline{\cdots}O)$ and $\nu(C\overline{\cdots}C\overline{\cdots}C)$ bands of **7a** and **7b** are quite similar to those of **5**, certifying the same bonding mode of the 2,4-pentanedionate ligand in these compounds. The ν(Pd–O)

Table II. Characteristic IR and Proton NMR Spectra of the η^3 2,4-Pentanedionato Complexes with Palladium(II)

	6	8a	8b	9a	9b	Assignment
IR, cm^{-1}	1643 vs	1630 vs	1633 vs	1631 vs	1633 vs	ν(C=O)
	1498 m	1523 m	1524 m	1529 m	1531 m	ν(C=C)
	505 s	*b*	505 s	505 m	507 m	ν(Pd-C)
	275 s					ν_b(Pd-Cl)
		290 s	291 s	287 s 270 s	292 s 275 s	ν_t(Pd-Cl)
NMR,[a] τ		7.56	7.60	7.70	7.73	CH_3
		7.52	7.46	7.70	7.73	CH_2
		5.51[c]	5.63	6.22	6.22	CH
		−2.80	−2.36	−1.30	−1.28	OH

[a] Recorded at 100 MHz in $CDCl_3$ using Me_4Si as an internal reference. [b] Masked by the PPh_3 bands. [c] Doublet with J_{P-H} = 8 Hz.

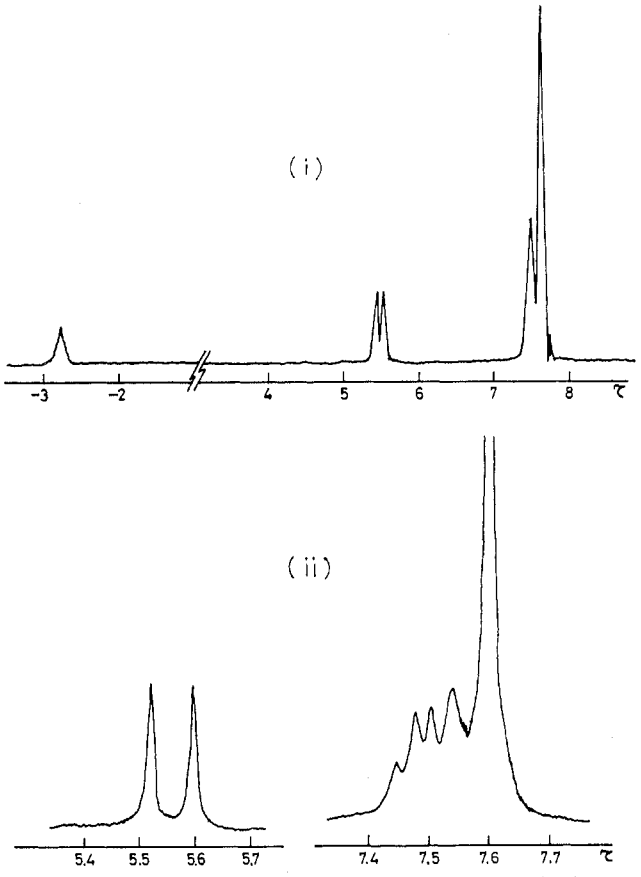
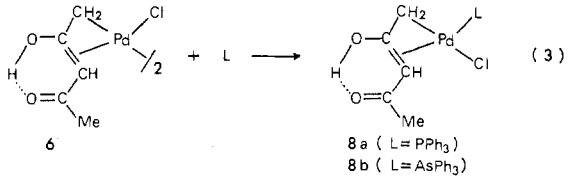


Figure 1. Proton NMR spectra at 100 MHz of $PdCl(acac\text{-}C^1\text{-}C^3)PPh_3$ in $CDCl_3$ at room temperature (i) and in CD_2Cl_2 at −60 °C (ii) with Me_4Si as an internal reference.

frequencies are a little lower as compared with that of **5** probably because of higher trans influence of the phosphine and arsine ligands. On the other hand the ν(Pd–Cl) bands are observed in the frequency region reasonable for the terminal Pd–Cl linkage. These IR spectra together with the observed molecular weight are in accordance with the mononuclear structure of **7a** and **7b** and may also support the binuclear structure of the parent compound **5**.

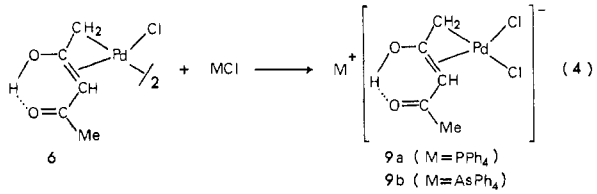
η^3-2,4-Pentanedionato Complexes. Compound **6** gives the same analytical data as **5** but exhibits a very strong IR band at 1643 cm^{-1} and a medium band at 1498 cm^{-1} (Table II). Such a spectral pattern is quite different from that of **5**, revealing that the 2,4-pentanedionate ligand in **6** is not O,O′ chelated to the metal atom. The spectrum of **6** in the lower frequency region closely resembles that of the η-allylic palladium(II) complex of ethyl acetoacetate **2** except that a strong band is observed at 505 cm^{-1} instead of a band at 545 cm^{-1} for **2**. The latter 545-cm^{-1} band was assigned[3a] to δ(CCC) in accordance with literature.[13] On the other hand strong ν(Pd–C) bands also appear at about 540 cm^{-1} for the terminal-carbon-bonded complexes **4**[4a] and at 518–540 cm^{-1} for the central-carbon-bonded 2,4-pentanedionato complexes[6a] of the type **3**. Although it is not certain whether the 505-cm^{-1} band of **6** is attributable to δ(CCC) or to ν(Pd—C), the η^3 structure is tentatively presumed. The ν(C=O) band at 1643 cm^{-1} corresponds to that of the enol tautomer of acacH[14] at 1620 cm^{-1} and may suggest the existence of intramolecular or intermolecular hydrogen bonding with the enolic hydroxy group, supporting the η^3 structure as depicted in eq 1. The dimeric structure is ascertained by a strong band at 275 cm^{-1} attributable to the Pd–Cl(bridging) stretch, of which lower frequency compared with 323 cm^{-1} for **5** might be due to the trans influence of the carbon donor stronger than that of the oxygen donor in **5**. The IR spectrum of **6′** nearly coincides with that of **6** except the ν(Pd–Cl) band for the latter complex, indicating that compound **6′** has the same structure as **6**.

Insolubility of compound **6** in appropriate solvents prevents the unequivocal assignment of its structure. The bridge-splitting reactions (eq 3) with triphenylphosphine or tri-



(3)

phenylarsine in benzene afforded soluble mononuclear complexes **8a** and **8b**, respectively. A similar bridge splitting of **6** with lithium chloride followed by the cation exchange with tetraphenylphosphonium and tetraphenylarsonium chlorides gave the anionic complexes **9a** and **9b**, respectively.

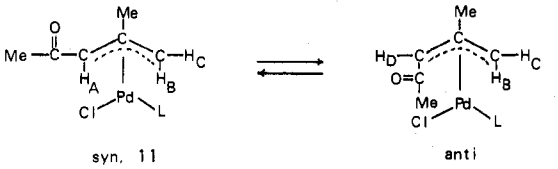


(4)

As is seen in Table II the characteristic IR bands of **8a**, **8b**, **9a**, and **9b** coincide with each other, and also nearly with those of the parent compound **6**, substantiating the maintenance of the same linkage mode of acacH in these reactions. The ν(Pd–Cl) frequency is rather low for the terminal chloride in either complex, and may be caused again by the strong trans influence of the carbon donor. Of the two ν(Pd–Cl) bands observed for either of **9a** and **9b**, the lower frequency band may be assigned to the Pd–Cl bond trans to the terminal methylene ligand which exerts stronger trans influence as compared to the olefin.

The analytical and molecular weight data for complexes **8** and **9** indicate unequivocally that the 2,4-pentanedionate anion is functioning as a bidentate ligand. The η^3 bonding as de-

Table III. Proton Resonances of Syn and Anti Isomers of Compound **11** (from Ref 18)



Config	L	τ_A	τ_B	τ_C	τ_D	J, Hz
Syn	PPh_3	5.69	7.72	6.34		$P-H_A \simeq 10$, $P-H_B \simeq 2$
Syn	$AsPh_3$	5.7	7.65	6.17		
Anti	PPh_3		7.72	6.34	4.69	$P-H_D \simeq 10$, $P-H_B \simeq 2$
Anti	$AsPh_3$		7.65	6.17	4.4	

picted in eq 3 and 4 is tentatively proposed on the basis of the proton NMR spectra summarized in Table II. As is seen in Figure 1(i) the proton signals of the 2,4-pentanedionate moiety in **8a** are composed of three singlets at τ 7.56 (3 H), 7.52 (2 H), and −2.80 (1 H) and a doublet at τ 5.51 (1 H) which are easily attributed to the acetyl methyl, terminal methylene, enolic proton, and vinyl proton, respectively, based on the proposed structure. The signal at the lowest field readily disappears on exchange with D_2O, supporting the assignment to the enolic proton. Its appearance at the remarkably low field indicates the effect of intramolecular hydrogen bonding with the carbonyl group as suggested by the IR spectrum. Splitting of the vinyl proton is caused by the coupling with ^{31}P of the triphenylphosphine ligand, and the J_{P-H} value of 8 Hz may reflect their positions trans to each other.

In recent years the structures of various η-allylic complexes in solution have been studied quite extensively by means of NMR spectroscopy.[15] In asymmetrically substituted η-allylic complexes, the carbon atom with a substituent has a tendency to be aligned trans to the better labilizer.[16] Furthermore the terminal-substituted η-allylic complex prefers the syn configuration although the bulky substituent attached to the central carbon of the allyl moiety increases the proportion of anti isomer in solution. Thus chloro-1-3-η-(1-acetylallyl)-(pyridine)palladium(II) exists solely as a syn isomer in a 3:1 deuteriochloroform–benzene solution at room temperature, whereas chloro-1-3-η-(1-acetyl-2-methylallyl)(pyridine)palladium(II) consists of both syn and anti isomers, the latter being the major component.[17]

The NMR data of chloro-1-3-η-(1-acetyl-2-methylallyl)-(triphenylphosphine or triphenylarsine)palladium(II) reported by Fong and Kitching[18] are more informative for us. Both of these compounds exist as an equilibrium mixture of syn and anti isomers in the ratio of 1:4 in deuteriochloroform at 34 °C, exhibiting the proton resonances given in Table III. The NMR spectrum of the present complex displayed in Figure 1 consists of one set of resonances, revealing that it exists solely as one isomer syn which is stabilized overwhelmingly by the intramolecular hydrogen bonding. In fact the chemical shift of the vinyl proton (τ 5.51) coincides well with that of the anti proton H_A (τ 5.69) in the corresponding 2-methylallyl complex **11** although the value of J_{P-H} (8 Hz) is slightly lower than that in **11** (10 Hz).

A serious discrepancy between the spectra of **8** and **11** is manifested by the terminal methylene protons. Usually the syn and anti protons in η-allylic complexes show an appreciable difference in the chemical shift. Thus the resonances of H_B and H_C in **11** are more than 1 ppm apart from each other. On the contrary the methylene protons in the present complex **8a** resonate at τ 7.52 as a single peak at room temperature. The spectrum of **8b** bears a close resemblance to that of **8a**, and the anionic complexes **9** also exhibit quite similar spectra except that the methyl and methylene resonances coincide with each other to result in a 5 H signal. The equivalence of the

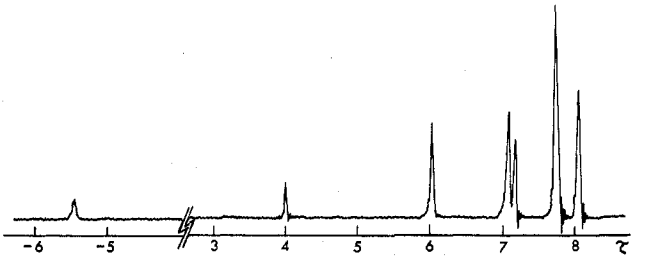


Figure 2. Proton NMR spectrum at 100 MHz of PdCl(acac-C^1)(bpy) in $CDCl_3$ with Me_4Si as an internal reference.

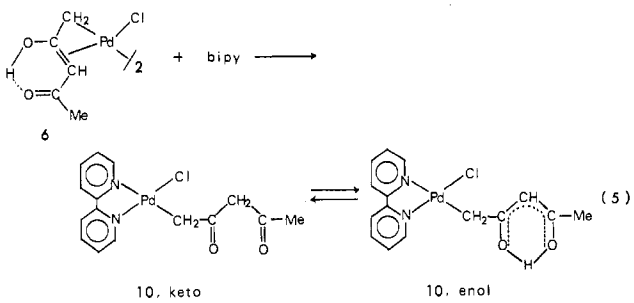
end methylene protons in these complexes seems to be caused by their dynamic behavior.

The temperature-dependent NMR spectra of PdO-$COCH_3$(η^3-2-methylallyl)PPh_3 showed that signals of protons cis to the phosphine ligand begin to broaden at about −30 °C and collapse at about 0 °C although such a syn–anti interchange was not observed in the corresponding chloro complex.[19] With the lowering of temperature the end-methylene singlet of **8a** becomes broad and then splits into a multiplet. Figure 1(ii) reproduces the spectrum of **8a** in dichloromethane-d_2 at −60 °C. The methyl singlet and the methine doublet are invariably sharp, indicating the maintenance of the CH–P coupling. The methylene multiplet appears to be composed of a quartet centered at τ 7.49 and a broad singlet (or possibly a triplet) at τ 7.55. This cannot be reasonably interpreted at present, but it is certain that the usual η-allylic bonding is not realized. The localized η^3 bonding scheme is tentatively shown in eq 1, 3, and 4 in order to differentiate the present bonding mode from the delocalized η-allylic bonding.

The intervention of such a localized η^3 structure has been presumed in the mechanism of syn–anti interchange of asymmetric η-allylic complexes.[15,20] Appreciably localized bonding of the allylic moiety was also disclosed by the x-ray analysis of PdCl(η^3-2-methylallyl)PPh_3,[21] Pd(SDBM)(η^3-2-methylallyl),[22] and Pd(SDBM)(η^3-1-*tert*-butyl-2-methylallyl)[23] where SDBM stands for the monothiodibenzoylmethanate ion. However, the present complexes might be an example of a completely localized allylic system. The unique structure seems to be stabilized by the hydrogen chelate ring including two conjugate double bonds, since the characteristic spectral behavior is displayed by **8** and **9** irrespective of nature of the coexisting ligand L, but not by **11** which carries the methyl substituent at the central carbon in place of the hydroxy group. Magnetic equalization of the methylene protons in **8** and **9** at room temperature may be accomplished by fluctuation of the dihedral angle between the ligand plane and the coordination plane around the metal atom.

It seems worth noting here that the complexes **8a** and **8b** are the linkage isomers of **7a** and **7b**, respectively, although another pair of **5** and **6** needs further characterization. Linkage isomerism is usually concerned with the ambidentate ligands which can coordinate to a metal atom through different donor atoms.[24] Now 2,4-pentanedione manifests two different bonding patterns, O,O′ chelation and η^3 C^1–C^3 bonding, exhibiting a novel type of isomerism. It is quite interesting that **6** seems to be more stable than **5** since **6** is produced via **5**. The equilibrium and kinetics of isomerization between **7a** and **8a** and between **7b** and **8b** deserve further investigations.

The Terminal-Carbon-Bonded Complex. The reaction of **6** with 2,2′-bipyridine in chloroform afforded the terminal-carbon-bonded complex of acacH **10**. As is seen in Figure 2 the proton NMR spectrum of **10** is composed of seven resonances except those due to the bipyridine-ring protons and is rationalized on the basis of the keto–enol tautomerism of terminal-carbon-bonded acac (eq 5). Three signals at τ 7.71,



7.06, and 6.04 show the intensity ratio 3:2:2 and are ascribed to CH_3, terminal CH_2, and central CH_2 protons, respectively, of the keto tautomer. The remaining four signals at τ 8.05, 7.13, 4.00, and −5.47 have the intensity ratio 3:2:1:1, assigned to CH_3, CH_2, CH, and OH protons, respectively, of the enol tautomer. These values of chemical shift nearly coincide with those reported for free acacH tautomers[25] except for the terminal methylenes bonded to palladium. Signals ascribed to the central methylene of keto tautomer and methine and hydroxy protons of enol tautomer disappear on exchange with D_2O in accordance with the proposed structure.

The terminal carbon bonding of acacH has been recognized only in $TeCl_2(acac\text{-}C^1)_2$,[26] and the present complex is the first example of transition metal compounds. The area ratio of two methyl signals gives the equilibrium quotient Q = [enol]/[keto] = 0.7 for the two tautomers in $CDCl_3$ at 25 °C, and the value does not change appreciably between −20 and +40 °C. Free acacH favors the enol form, Q being 6.7 in chloroform at 33 °C.[27] In general an electron-attracting substituent on acacH increases Q, while an electron-releasing substituent exerts the opposite effect. Thus Q is 32 for 1,1,1-trifluoro-2,4-pentanedione and 0.43 for 3-methyl-2,4-pentanedione as neat liquids at 33 °C.[28] The present result together with the previous observation[6a] that the central-carbon-bonded acac in Pd(acac-*O*,*O*′)(acac-C^3)L has solely the keto form clearly indicates that the palladium(II) atom is strongly electron donating as a substituent on acacH.

Coexistence of keto and enol tautomers in a solid specimen of **10** is revealed by the IR spectrum in Nujol. Together with a medium ν(Pd—C) band at 530 cm^{-1} and a strong ν_t(Pd—Cl) band at 330 cm^{-1}, two strong bands are observed at 1723 and 1630 cm^{-1}. The former is assigned to the ν(C=O) vibration in the keto tautomer, while the latter is considered to be a combination of ν(C···O) and ν(C···C···C) vibrations in the enol tautomer. The relative intensities of these two bands alter with the solvent in which the bridge splitting reaction (eq 5) was conducted. The [enol]/[keto] ratio in solid diminishes with increasing polarity of the solvent in the sequence of benzene, dichloromethane, chloroform, and nitromethane. When a specimen prepared in dichloromethane was dissolved in chloroform, the ν(C=O) band at 1723 cm^{-1} grew with time at the expense of the 1630-cm^{-1} band to attain an equilibrium after about 30 min. The tautomeric equilibrium of the metal-bonded acacH seems to depend on the solvent polarity in a similar fashion as free acacH does.

The central-carbon-bonded acac has the keto form exclusively, reserving the ability of further coordination to another metal ion[29] in a similar fashion as a keto tautomer of molecular acacH coordinates to various metal ions.[8] On the other hand the terminal-carbon-bonded acac still retains an ionizable proton and has the possibility of enolate chelate formation with another metal ion. The η^3-allylic complexes **8** and **9** also have the enolic proton and may be expected to form a novel type of dinuclear complex although it is questionable whether the η^3 bonding of acac with palladium(II) could be maintained during the reactions. Preparative studies of these dinuclear complexes of palladium(II) and another metal ion containing a 2,4-pentanedionate dianion as a bridging ligand are now in progress.

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Registry No. **5**, 65027-68-1; **6**, 65027-69-2; **6′**, 65027-70-5; **7a**, 52596-06-2; **7b**, 65027-71-6; **8a**, 59400-24-7; **8b**, 59589-18-3; **9a**, 59400-26-9; **9b**, 65036-09-1; **10**, 59588-96-4; $PdCl_2(PhCN)_2$, 14220-64-5; $PdBr_2(PhCN)_2$, 15003-43-7.

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