2–3 h. The reaction mixture was evaporated to dryness, the solid was taken up in methylene chloride, and the products were separated by thin-layer chromatography on silica gel by using 1:19 ether–hexane as eluant. For R = C_6H_5, five to six bands were separated: (1) unreacted I, 10–15%, (2) unreacted phosphine, (3) III, 210–240 mg (40–55%), (4) IV, 50–60 mg (10–15%), (5) pale yellow band in a trace amount not identified, and (6) red band (toluene reaction only) also in trace amounts not identified. (Yields given are on bands extracted with CH_2Cl_2.) Products III and IV were recrystallized from heptane. Similar yields are obtained by using this procedure for R = OCH_3.

Reaction of IIa with $(C_6H_5)_3P$. A 150-mg (0.241-mmol) sample of IIa, 65 mg (0.248 mmol) of $(C_6H_5)_3P$, and 175 mL of cyclohexane were combined in a 250-mL three-necked flask and refluxed with magnetic stirring for 2 h. The reaction mixture was evaporated to dryness, the solid was taken up in dichloromethane, and the products were separated by TLC on silica gel by using 1:9 ether–hexanes as eluant. Four bands were separated: (1) unreacted IIa, 5 mg, (2) V, 65 mg (31.4% yield), (3) orange band in a trace amount not identified, and (4) yellow-orange band, 8 mg, not identified (yields given on bands extracted with CH_2Cl_2). Product V was recrystallized from ether–heptane at −20 °C.

Reaction of IIb with $(C_6H_5)_3P$. A 60-mg (0.096-mmol) sample of IIb, 25 mg (0.096 mmol) of $(C_6H_5)_3P$, and 60 mL of cyclohexane were combined in a 100-mL three-necked flask and refluxed with magnetic stirring for 2 h. The reaction mixture was evaporated to dryness, the solid was taken up in methylene chloride, and the components were separated by TLC on silica gel by using 8% ether in hexanes as eluant. Five bands were separated: (1) unreacted IIb, 7 mg, (2) VI, 20 mg (24% yield), (3) orange band in a trace amount not identified, (4) yellow band in a trace amount not identified, and (5) reddish orange band in a trace amount not identified (yields given on bands extracted with CH_2Cl_2). Product VI was recrystallized from chloroform–hexanes at −20 °C.

Acknowledgment. We thank the donors of Petroleum Research Fund, administered by the American Chemical Society, the Research Corp., the CNR–NSF International Science Program, and the North Atlantic Treaty Organization for support of this research. We also thank Dr. K. L. Servis, University of Southern California, and Dr. T. Fratiello, California State University at Los Angeles, for the use of NMR equipment at their respective universities and Mathey-Bishop, Ltd., for a loan of $RuCl_3 \cdot 3H_2O$.

Registry No. I, 57673-31-1; IIa, 56943-13-6; IIb, 57327-10-3; III (R = C_6H_5), 72582-02-6; III (R = OCH_3), 72582-03-7; IV (R = C_6H_5), 72582-04-8; IV (R = OCH_3), 72599-26-9; V, 72708-35-1; VIa, 72582-05-9; VIb, 72582-06-0; $Ru_3(CO)_{12}$, 15243-33-1; $(CH_3)_3CC{\equiv}CH$, 917-92-0; isoprene, 78-79-5; 1,3-pentadiene, 504-60-9.

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η^3-β-Diketonato(2–) Complexes of Palladium(II)

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Received October 3, 1979

The palladium(II) complexes containing dianions of acetylacetone and ethyl acetoacetate, [Pd(acac(2–)-C^1–C^3)(NN)] and [Pd(etac(2–)-C^1–C^3)(NN)], where NN is 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, or 1,10-phenanthroline, have been prepared by the reactions of the corresponding terminal-carbon-bonded complexes of the β-dicarbonyl compounds with thallium(I) acetylacetonate as a base. The η^3 coordination of the β-diketonate dianions in these complexes was confirmed by analytical, IR, and NMR measurements.

The η^3 carbon-bonded complex of acetylacetone with palladium(II) [PdCl(acac-C^1–C^3)]$_2$ (**1**) was prepared by the reaction of dichlorobis(benzonitrile)palladium(II) with acetylacetone in acetone at room temperature and reacted with 2,2′-bipyridine to afford the η^1 complex [PdCl(acac-C^1)(bpy)] (**3a**).[1] Similarly the η^3 palladium(II) complex of ethyl acetoacetate [PdCl(etac-C^1–C^3)]$_2$ (**2**) was obtained from the ethanolysis of diketene in the presence of the tetrachloropalladate(II) and was also prepared by the direct reaction of palladium(II) chloride with the keto ester.[2] The bridge-splitting reaction of **2** with 2,2′-bipyridine yielded [PdCl(etac-C^1)(bpy)] (**4a**).[3]

The acetylacetone terminal carbon bonded to palladium(II) in **3a** still contains the ionizable methylene protons, and it reacted with other metal compounds to produce the dinuclear and trinuclear complexes in which the acetylacetonate dianion is working as a C,O,O′-bridging ligand.[4] It was supposed that thallium(I) acetylacetonate might displace the chloride ion in **1** and **2** to produce the palladium(II) complexes containing two kinds of unidentate β-diketonate anions, one the terminal carbon bonded and the other the central carbon bonded or otherwise oxygen bonded. In fact the reactions occurred easily at room temperature, but contrary to expectation, the products were the palladium(II) complexes containing the β-diketonate dianion. This paper reports on these novel types of complexes.

Experimental Section

η^3 Complexes of Monoanions of Acetylacetone and Ethyl Acetoacetate with Palladium(II). Di-μ-chloro-bis(η^3-1-acetyl-2-hydroxyallyl)dipalladium(II), [PdCl(acac-C^1–C^3)]$_2$ (**1**), was prepared by the reported method.[1] Di-μ-chloro-bis(η^3-1-ethoxycarbonyl-2-hydroxyallyl)dipalladium(II), [PdCl(etac-C^1–C^3)]$_2$ (**2**), was prepared by the following method originally proposed by Tezuka.[2] Ethyl acetoacetate (10 mL) was added with stirring to a suspension of palladium(II) chloride (1.10 g, 6.20 mmol) in water (80 mL) at 70 °C. A brown precipitate appeared promptly, which was filtered after 1 h of stirring, washed with water until the washings were no longer colored, and dried in vacuo. The filtrate combined with the washings was left standing at room temperature for 9 days to deposit another crop of the product which showed the same IR spectrum as that of the above precipitate. The total yield of the crude product was 1.42 g (85%), which was dissolved in hot benzene. After filtration, the solution was

(1) Kanda, Z.; Nakamura, Y.; Kawaguchi, S. *Inorg. Chem.* **1978**, *17*, 910.
(2) Tezuka, Y.; Ogura, T.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 443.
(3) Baba, S.; Sobata, T.; Ogura, T.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2792.
(4) Yanase, N.; Nakamura, Y.; Kawaguchi, S. *Inorg. Chem.* **1978**, *17*, 2874.

0020-1669/80/1319-1575$01.00/0

concentrated by evaporation and deposited a precipitate on addition of petroleum ether.

Bridge-splitting reaction of **2** with an equivalent amount of pyridine gave a mononuclear complex [PdCl(etac-C^1–C^3)(py)] preserving the η^3 linkage of ethyl acetoacetate to the metal atom.[3] As an extension of this study, the following mononuclear η^3 complexes of the ester ligand have been prepared.

[PdCl(etac-C^1–C^3)(PPh_3)] (2a). A dichloromethane solution (5 mL) of triphenylphosphine (0.200 g, 0.762 mmol) was added dropwise to a suspension of **2** (0.206 g, 0.380 mmol) in dichloromethane (3 mL) to result in a clear yellow solution. After being stirred for 20 min at room temperature, the solution was concentrated to ca. 2 mL by evaporation under reduced pressure. On slow addition of diethyl ether to the concentrate, yellow crystals precipitated, which were filtered, washed twice with 5-mL portions of diethyl ether, and dried in vacuo. The yield was 88% (0.356 g).

PPh_4[$PdCl_2$(etac-C^1–C^3)] (2b) and $AsPh_4$[$PdCl_2$(etac-C^1–C^3)] (2c). In a similar manner as above the reaction of **2** (0.117 g, 0.215 mmol) with tetraphenylphosphonium chloride (0.162 g, 0.431 mmol) in dichloromethane gave orange crystals of **2b** in a 93% yield (0.260 g), and the reaction of **2** (0.101 g, 0.186 mmol) with tetraphenylarsonium chloride (0.156 g, 0.372 mmol) produced orange crystals of **2c** in a 94% yield (0.242 g).

Preparation of the Terminal-Carbon-Bonded Complexes of Acetylacetone and Ethyl Acetoacetate with Palladium(II). Acetylacetonato-C^1-(2,2′-bipyridine)chloropalladium(II), [PdCl(acac-C^1)(bpy)] (**3a**),[1] and the corresponding ethyl acetoacetato complex [PdCl(etac-C^1)(bpy)] (**4a**)[3] were prepared by the reported methods and purified by reprecipitation from chloroform–diethyl ether and dichloromethane–diethyl ether, respectively.

[PdCl(acac-C^1)(Me_2bpy)] (3b). A chloroform solution (5 mL) of 4,4′-dimethyl-2,2′-bipyridine (0.138 g, 0.750 mmol) was added dropwise to a suspension of **1** (0.174 g, 0.361 mmol) in chloroform (10 mL) and stirring was continued for ca. 15 min at room temperature. After filtration the filtrate was concentrated to ca. 10 mL by evaporation under reduced pressure. Diethyl ether was added to the concentrate to obtain a yellow precipitate in a 96% yield (0.295 g), which was purified by reprecipitation from chloroform–diethyl ether.

[PdCl(acac-C^1)(phen)] (3c). A chloroform solution (10 mL) of 1,10-phenanthroline hydrate (0.175 g, 0.881 mmol) was added drop by drop to a suspension of **1** (0.205 g, 0.425 mmol) in chloroform (10 mL) with stirring at room temperature. The amount of suspended starting complex decreased gradually with the progress of reaction and instead a bright yellow precipitate appeared. After stirring of the mixture for 30 min, about 100 mL of chloroform was added, and the mixture was heated in order to dissolve the yellow precipitate completely. The solution was filtered and the filtrate was concentrated to ca. 10 mL by evaporation under reduced pressure. Diethyl ether was added to the concentrate to obtain **3c** in a 94% yield (0.337 g), which was purified by reprecipitation as above.

[PdCl(etac-C^1)(Me_2bpy)] (4b) and [PdCl(etac-C^1)(phen)] (4c). A dichloromethane solution (5 mL) of Me_2bpy (0.113 g, 0.612 mmol) was added dropwise to a suspension of **2** (0.152 g, 0.281 mmol) in dichloromethane (5 mL) with stirring at room temperature to result in a transparent yellow solution. After 20 min of being stirred the mixture was filtered and the filtrate was concentrated to ca. 2 mL. Diethyl ether was added to the concentrate to obtain a yellow precipitate of **4b** in a 97% yield (0.249 g). Complex **4c** was also prepared in a similar fashion by the reaction of **2** (0.181 g, 0.334 mmol) with phen·H_2O (0.136 g, 0.684 mmol). The yield was 97% (0.249 g). Both complexes were purified by reprecipitation from dichloromethane–diethyl ether.

Preparation of the Palladium(II) Complexes Containing Dianions of Acetylacetone and Ethyl Acetoacetate as a Ligand. (η^3-Acetylacetonato(2−))(2,2′-bipyridine)palladium(II), [Pd(acac(2−)-C^1–C^3)(bpy)] (5a). A suspension of **3a** (0.122 g, 0.308 mmol) and thallium(I) acetylacetonate[5] (0.151 g, 0.496 mmol) in benzene (15 mL) was stirred for 5 h at room temperature to produce a pale yellow precipitate, which was filtered and washed twice with 5-mL portions of hot benzene to remove excess Tl(acac). The precipitate was dissolved in dichloromethane (10 mL) and insoluble thallium(I) chloride was filtered off. A yellow solution was vaporized to ca. 2 mL under reduced pressure and diethyl ether was added to the concentrate to obtain a yellow precipitate of **5a** in a 93% yield (0.104 g), which was recrystallized from dichloromethane–diethyl ether.

[Pd(acac(2−)-C^1–C^3)(Me_2bpy)] (5b) and [Pd(acac(2−)-C^1–C^3)(phen)] (5c). The reaction of **3b** (0.178 g, 0.419 mmol) with Tl(acac) (0.137 g, 0.451 mmol) and that of **3c** (0.173 g, 0.410 mmol) with Tl(acac) (0.131 g, 0.432 mmol) were carried out in a similar fashion as above to obtain yellow precipitates of **5b** and **5c** in 97% (0.158 g) and 67% (0.106 g) yields, respectively, both of which were recrystallized from methanol–diethyl ether.

[Pd(etac(2−)-C^1–C^3)(bpy)] (6a). A dichloromethane solution (10 mL) of **4a** (0.315 g, 0.737 mmol) was added dropwise to a suspension of Tl(acac) (0.225 g, 0.743 mmol) in dichloromethane (5 mL). The mixture was stirred for 2 h and filtered. The precipitate was washed with dichloromethane (3 mL), and the filtrate combined with the washings was evaporated to 5 mL under reduced pressure. Diethyl ether was added to the concentrate to obtain a yellow precipitate of **6a** in a 97% yield (0.280 g), which was purified by reprecipitation from dichloromethane–diethyl ether.

[Pd(etac(2−)-C^1–C^3)(Me_2bpy)] (6b) and [Pd(etac(2−)-C^1–C^3)(phen)] (6c). The reactions of **4b** (0.150 g, 0.329 mmol) with Tl(acac) (0.102 g, 0.337 mmol) in dichloromethane and of **4c** (0.173 g, 0.384 mmol) with Tl(acac) (0.131 g, 0.432 mmol) in benzene were performed in a similar manner as above to obtain yellow precipitates of **6b** and **6c** in 98% (0.136 g) and 99% (0.158 g) yields, respectively. Both of them were purified by reprecipitation.

Preparation of the (η^3-1-Ethoxycarbonyl-2-hydroxyallyl)(2,2′-bipyridine)palladium(II) Salts. [Pd(etac-C^1–C^3)(bpy)]ClO_4 (7a). An acetone solution (5 mL) of silver perchlorate (0.210 g, 1.01 mmol) was added dropwise to a suspension of **2** (0.226 g, 0.416 mmol) in acetone (4 mL). After stirring of the mixture for 2 h at room temperature a white precipitate of silver chloride was separated by filtration and washed twice with 3-mL portions of acetone. The filtrate was combined with the washings and evaporated to dryness under reduced pressure. The residue was treated with chloroform (3 mL) and excess silver perchlorate was filtered off. A chloroform solution (2 mL) of 2,2′-bipyridine (0.132 g, 0.843 mmol) was added with stirring to the filtrate in an ice bath to produce a pale yellow precipitate promptly. After 20 min of stirring of the mixture, the precipitate was filtered, washed with small portions of chloroform and diethyl ether successively, and dried in vacuo. The yield was 97% (0.399 g).

[Pd(etac-C^1–C^3)(bpy)]BPh_4 (7b). A suspension of **7a** (0.114 g, 0.233 mmol) and sodium tetraphenylborate (0.080 g, 0.233 mmol) in dichloromethane (6 mL) was stirred for 30 min in an ice bath and then filtered. Diethyl ether (10 mL) was quickly added to the combined filtrate and washings to separate out a pale yellow precipitate of **7b** in an 89% yield (0.148 g), which was filtered, washed with diethyl ether, and dried in vacuo. Solution of **7b** in dichloromethane is rather stable at temperatures lower than 0 °C but decomposes rapidly at room temperature to produce a black precipitate.

Reactions of [Pd(etac-C^1–C^3)(bpy)]ClO_4 (7a) with Bases. Addition Reaction of Triethylamine with 7a to Form [Pd(etac·NEt_3-C^1–C^3)(bpy)]ClO_4 (7c). An excess amount of triethylamine (0.100 g, 0.990 mmol) was added slowly to a suspension of **7a** (0.065 g, 0.13 mmol) in cold dichloromethane (5 mL), and the mixture was stirred for 20 h at −15 °C. The yellow solution was evaporated to 2 mL under reduced pressure, and diethyl ether was added to the concentrate to deposit a yellow precipitate of **7c** in a 98% yield (0.075 g), which was filtered, washed with ether, and dried in vacuo.

Reaction of 7a with γ-Picoline to Produce [Pd(etac-C^1)(γ-pic)(bpy)]ClO_4 (4d). A benzene solution (3.6 mL) of γ-picoline (0.103 g, 1.11 mmol) was added slowly to a suspension of **7a** (0.181 g, 0.369 mmol) in dichloromethane (8 mL) to result in a clear yellow solution. After stirring of the mixture for 20 h, the solution was evaporated to 2 mL under reduced pressure and diethyl ether was added to the concentrate to separate out a yellow oily substance, which was dissolved in methanol (3 mL) and kept in a refrigerator overnight to precipitate needles. The crystals were filtered, washed with 3-mL portions of methanol and diethyl ether successively, and dried in vacuo. The yield was 73% (0.157 g).

Reaction of 7a witb Potassium Acetylacetonate to Produce 6a. A methanol solution (2 mL) of potassium acetylacetonate (0.051 g, 0.37 mmol) was added to a suspension of **7a** (0.123 g, 0.250 mmol) in cold methanol (3 mL). After stirring of the mixture for 20 h at −15 °C, a white precipitate of potassium perchlorate was filtered and washed with methanol (2 mL). The filtrate and washings were combined and

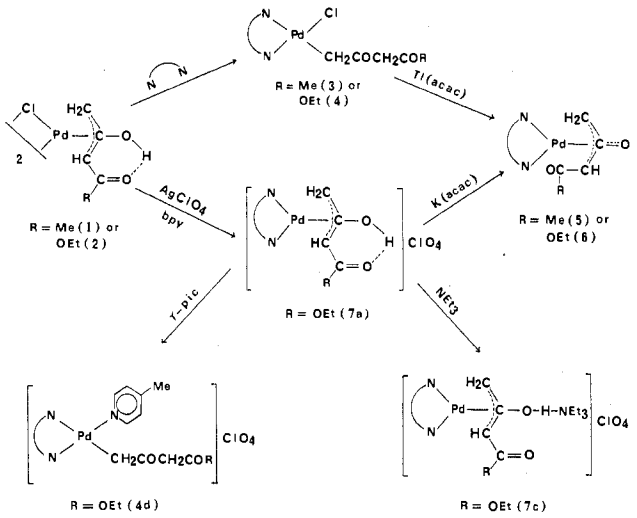
(5) Prepared by the method of: Nelson, W. H.; Randal, W. J.; Martin, D. F. *Inorg. Synth.* **1967**, *9*, 52.

Table I. Analytical Data for the Newly Prepared Complexes

no.	complex	% C		% H		% N		mol wt[a]	
		calcd	found	calcd	found	calcd	found	calcd	found
2a	$[PdCl(etac\text{-}C^1\text{-}C^3)(PPh_3)]$	54.06	53.81	4.54	4.55				
2b	$PPh_4[PdCl_2(etac\text{-}C^1\text{-}C^3)]$	55.79	54.89	4.53	4.49				
2c	$AsPh_4[PdCl_2(etac\text{-}C^1\text{-}C^3)]$	52.24	51.44	4.24	4.19				
3b	$[PdCl(acac\text{-}C^1)(Me_2bpy)]$	48.02	47.32	4.50	4.38	6.59	6.53	425	423
3c	$[PdCl(acac\text{-}C^1)(phen)]$	48.48	47.64	3.59	3.46	6.65	6.60		
4b	$[PdCl(etac\text{-}C^1)(Me_2bpy)]$	47.49	47.48	4.65	4.59	6.15	6.08	455	459
4c	$[PdCl(etac\text{-}C^1)(phen)]$	47.92	47.74	3.80	3.75	6.21	6.13	451	459
4d	$[Pd(etac\text{-}C^1)(\gamma\text{-pic})(bpy)]ClO_4$	45.22	44.85	4.14	4.18	7.19	7.05	584	562
5a	$[Pd(acac(2-)\text{-}C^1\text{-}C^3)(bpy)]$	49.95	49.32	3.91	3.83	7.77	7.69	361	392
5b	$[Pd(acac(2-)\text{-}C^1\text{-}C^3)(Me_2bpy)]$	52.53	52.13	4.67	4.59	7.21	7.10	389	378
5c	$[Pd(acac(2-)\text{-}C^1\text{-}C^3)(phen)]\cdot H_2O$	50.70	50.50	4.00	3.96	6.96	6.96		
6a	$[Pd(etac(2-)\text{-}C^1\text{-}C^3)(bpy)]\cdot{}^1/_2H_2O$	47.13	47.41	4.20	4.19	6.87	6.86		
6b	$[Pd(etac(2-)\text{-}C^1\text{-}C^3)(Me_2bpy)]\cdot{}^1/_2CH_2Cl_2$	48.18	47.89	4.59	4.56	6.07	5.89	419	417
6c	$[Pd(etac(2-)\text{-}C^1\text{-}C^3)(phen)]\cdot{}^1/_2CH_2Cl_2$	48.60	47.71	3.75	3.74	6.13	6.16	415	438
7a	$[Pd(etac\text{-}C^1\text{-}C^3)(bpy)]ClO_4$	39.13	38.86	3.49	3.36	5.70	5.80		
7b	$[Pd(etac\text{-}C^1\text{-}C^3)(bpy)]BPh_4$	67.58	66.55	5.25	5.13	3.94	3.80		
7c	$[Pd(etac\cdot NEt_3\text{-}C^1\text{-}C^3)(bpy)]ClO_4$	44.61	44.55	5.45	5.40	7.09	7.07		

[a] Determined in dichloromethane (0.005–0.01 mol/L) at 25 °C.

Scheme I



evaporated to dryness under reduced pressure. The residue was treated with dichloromethane (5 mL) and insoluble excess potassium acetylacetonate was filtered and washed with dichloromethane (2 mL). The filtrate and washings were combined and concentrated to 1 mL by evaporation under reduced pressure, and diethyl ether was added to the concentrate to obtain a yellow precipitate of **6a** in a quantitative yield (0.105 g). Potassium perchlorate and excess potassium acetylacetonate were also recovered quantitatively and identified by the IR assay.

Measurements. Infrared spectra were obtained in Nujol mull with JASCO IR-E (4000–650 cm^{-1}), Hitachi EPI-L (700–200 cm^{-1}), and JASCO DS 701G (4000–200 cm^{-1}) infrared spectrophotometers. Proton NMR spectra were recorded on a JNM MH 100 instrument using tetramethylsilane as an internal reference. Proton FT NMR spectra of less soluble complexes such as **3c**, **5c**, **7a**, and **7b** and ^{13}C NMR spectra were taken with a JEOL FX-100 spectrometer. Molecular weight was determined in dichloromethane at 27 °C with a vapor pressure osmometer manufactured by Knauer, West Berlin, West Germany.

Results and Discussion

Starting from the η^3 palladium(II) complexes of acetylacetone and ethyl acetoacetate, $[PdCl(acac\text{-}C^1\text{-}C^3)]_2$ (**1**) and $[PdCl(etac\text{-}C^1\text{-}C^3)]_2$ (**2**), several terminal-carbon-bonded mononuclear complexes of these ligands, **3a–c** and **4a–d**, were derived by the bridge-splitting reactions with the bidentate nitrogen bases such as 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, and 1,10-phenanthroline. In the reaction of **3a** with thallium(I) acetylacetonate, the thallium(I) ion certainly combined with the chloride ligand; however, the acetylacetonate anion did not coordinate to palladium(II), but acted as a base to abstract a proton from the terminal-carbon-bonded acetylacetonate ligand, giving rise to a complex of the acetylacetonate dianion, **5a**. Similar reactions were also carried out successfully with other terminal-carbon-bonded complexes of acetylacetone (**3b** and **3c**) and ethyl acetoacetate (**4a–c**), affording the corresponding dianion complexes **5b**, **5c** and **6a–c**, respectively, in high yields.

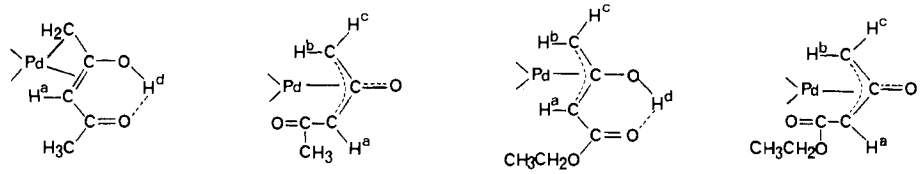
In order to verify the proposed mechanism, we derived compound **6a** from **2** via an alternative route. When the dinuclear complexes **1** and **2** were reacted with bases, the product mononuclear complexes retained the chloride owing to its high coordinating ability, and instead the η^3 β-diketonate ligand was converted into the η^1 state. On the other hand, replacement of the bridging chloride ligands in **2** with perchlorate anions followed by the bridge-splitting reaction with 2,2′-bipyridine gave a cationic mononuclear complex **7a** which reserves the η-allylic structure of the ester ligand. A similar reaction of **3a** was unsuccessful and only an O,O′-chelated product resulted.

The reactions of **7a** with several kinds of bases have been examined with the intention of abstracting the enolic hydrogen of **7a** to yield **6a**. γ-Picoline gave **4d** of which structure was confirmed by the analytical and spectral data. This base was so powerful as a ligand that it transformed the η^3 coordination of the ester ligand to the terminal carbon bonding. Triethylamine, on the other hand, could not abstract but coordinated to the enolic hydrogen in **2**, resulting in an interesting adduct **7c**. Potassium acetylacetonate proved to be the most appropriate base, accepting a proton from **7a** to afford **6a**.

The whole reaction pattern is summarized in Scheme I, and the analytical data for the newly prepared complexes are listed in Table I.

η^3 Complexes of the β-Diketonate Monoanions with Palladium(II). The ^1H NMR data for the η^3 complexes of β-diketonate mono- and dianions with palladium(II) are listed in Table II. Figure 1 shows the ^1H NMR spectrum of compound **2** in $CDCl_3$ which has not been reported and is reasonably interpreted on the basis of the η^3 structure confirmed by X-ray analysis.[6] The methyl and methylene protons of the ethyl group resonate as a triplet at 1.31 ppm and a multiplet centered at 4.29 ppm, respectively. The methylene protons in the acetoacetate ester coordinated to palladium as a η^3 ligand are diastereotopic and are environmentally nonequivalent,[7] man-

Table II. Proton NMR Data in CD_2Cl_2 for the η^3 Complexes of β-Diketonate Mono- and Dianions with Palladium(II)



no.	complex	chemical shift in ppm from internal Me_4Si						coupling constants in Hz
		CH_3	CH_3–CH_2	H^c	H^b	H^a	H^d	
1a	$PPh_4[PdCl_2(acac\text{-}C^1\text{-}C^3)]$	2.31			2.31	3.80	11.26	
5a	[Pd(acac(2–)-C^1-C^3)(bpy)]	2.40 (1.95)		2.55 dd (2.72)	2.71 d	3.71 d (4.98)		J(bc) = 4.4, J(ac) = 1.5
5b	[Pd(acac(2–)-C^1-C^3)(Me_2bpy)]	2.32 (1.92)		2.6[b] (2.70)	2.71 d	3.65 d (4.85)		J(bc) = 3.8
5c	[Pd(acac(2–)-C^1-C^3)(phen)]	2.43 (1.97)		2.67 dd (2.96)	2.74 dd	3.73 m (4.81)		J(bc) = 4.4, J(ac) = 1.6, J(ab) = 0.7
2	$[PdCl(etac\text{-}C^1\text{-}C^3)]_2$[a]		1.31 t 4.29 m	3.74 d	2.59 dd	3.59	10.46 d	J(bc) = 3.4, J(bd) = 1.2, $J(CH_3\text{-}CH_2)$ = 7.2
6a	[Pd(etac(2–)-C^1-C^3)(bpy)]		1.23 t 4.07 q	2.27 dd	3.02 d	3.53 d		J(bc) = 4.4, J(ac) = 2.3
6b	[Pd(etac(2–)-C^1-C^3)(Me_2bpy)]		1.17 t 4.03 q	2.24 dd	3.06 d	3.52 d		J(bc) = 3.8, J(ac) = 2.2
6c	[Pd(etac(2–)-C^1-C^3)(phen)]		1.26 t 4.14 q	2.43 dd	3.00 d	3.64 d		J(bc) = 4.0, J(ac) = 2.0
7a	$[Pd(etac\text{-}C^1\text{-}C^3)(bpy)]ClO_4$		1.51 t 4.51 m	3.83 d	3.36 dd	4.04	10.93 d	J(bc) = 3.7, J(bd) = 1.5
7b	$[Pd(etac\text{-}C^1\text{-}C^3)(bpy)]BPh_4$		1.50 t 4.46 m	3.57 d	2.99 d	3.63	11.1	J(bc) = 3.4
7c	$[Pd(etac\text{-}NEt_3\text{-}C^1\text{-}C^3)(bpy)]ClO_4$		1.26 t 4.14 q	3.72	2.68	c	6.57	

[a] In $CDCl_3$. [b] Overlapped by the methyl signal from Me_2bpy. [c] Overlapped by the methylene signal from NEt_3.

Table III. Carbon-13 NMR Chemical Shifts in Ppm from Internal Me_4Si in $CDCl_3$

no.	complex	CH_3	CH_3–CH_2	CH_2	CH	C–OH	C=O
1a	$PPh_4[PdCl_2(acac\text{-}C^1\text{-}C^3)]$	31.5		45.1	53.8	150.4	212.0
5a	[Pd(acac(2–)-C^1-C^3)(bpy)]	29.5		37.9	58.7	180.5	208.1
2	$[PdCl(etac\text{-}C^1\text{-}C^3)]_2$		14.5 62.3	46.4	47.7	152.0	175.4
6b	[Pd(etac(2–)-C^1-C^3)(Me_2bpy)]		14.6 59.2	36.5	48.7	180.0	172.1

ifesting the 16-line pattern owing to the chemical-shift difference of 20 Hz, geminal coupling of J = 11 Hz, and coupling to the methyl protons with J = 7.2 Hz.

Three signals assignable to the allylic protons are observed as a doublet of doublets, a singlet, and a doublet at 2.59, 3.59, and 3.74 ppm, respectively. Another 1.2-Hz doublet observed at 10.46 ppm disappeared on addition of D_2O, indicating that the signal is attributable to the enolic proton H^d which is linked to the carbonyl oxygen by the intramolecular hydrogen bonding. X-ray study of **2** revealed that the syn structure of the η-allylic ester ligand is forced by the intermolecular hydrogen bonds.[6] In the aprotic solvent such as chloroform the intermolecular association is broken, but instead the intramolecular hydrogen bonding preserves the syn structure.

The double doublet at 2.59 ppm was reduced to a doublet with J = 1.2 Hz by irradiation at 3.74 ppm and also to a doublet with J = 3.4 Hz on treating with D_2O. Thus the signal at 2.59 ppm is assigned to the anti proton H^b of the end methylene group and the 3.4-Hz doublet at 3.74 ppm to the syn proton H^c. The interaction between H^b and H^d across four bonds constituting a planar zigzag configuration accords with the so-called W rule.[8] The geminal coupling has scarcely been observed for the η-allylic systems, but the values of coupling constants reported for the $(\eta^3\text{-benzyl})Mo(CO)_2(\eta^5\text{-}C_5H_5)$ at

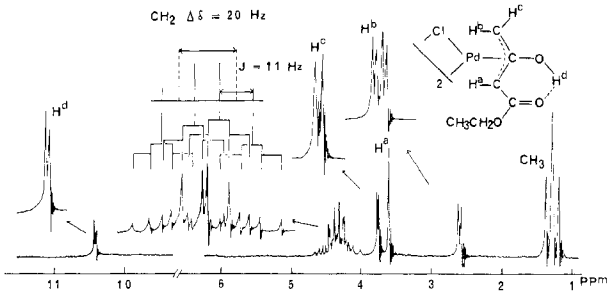


Figure 1. ^1H NMR spectrum of $[PdCl(etac\text{-}C^1\text{–}C^3)]_2$ (**2**) in $CDCl_3$ with internal Me_4Si.

−30 °C (3 Hz)[9] and the exocyclic η^3-allylic palladium(II) complexes of dehydro-3,4-dimethyl-2,5-di-*tert*-butylcyclopentadienone (2.4 Hz)[10] are comparable to the present value, $J(H^bH^c)$ = 3.4 Hz. The η^3 complex of acetoacetic acid with palladium(II) also gave the ^1H NMR spectrum in acetone-d_6 similar to that for the ester complex, the end methylene protons coupling to each other (J = 3 Hz).[11] The remaining singlet at 3.59 ppm is attributed to the methine proton H^a. Thus the chemical shifts of the allylic protons in the present complex, H^b (2.59 ppm), H^a (3.59 ppm), and H^c (3.74 ppm), nearly coincide with those (3.02, 3.58, and 3.71 ppm, respectively)

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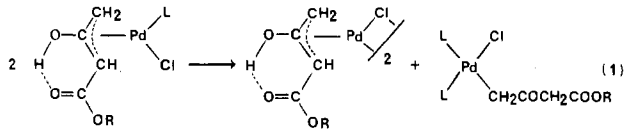
reported for the syn isomer of η^3-(1-acetyl-2-methallyl)-chloro(pyridine)palladium(II).[12] The ^{1}H NMR data for $PPh_4[PdCl_2(acac\text{-}C^1\text{-}C^3)]$ (**1a**) are also included in Table II for comparison. Signals for the end methylene and methyl protons cannot be distinguished from each other in this case.[1]

The ^{13}C NMR data for **1a** and **2** are listed in Table III. The spectrum of **1a** consists of five signals at 31.5 (CH_3), 45.1 (CH_2), 53.8 (CH), 150.4 (COH), and 212.0 (C=O) ppm. Assignment of the three higher field signals to the methyl, methylene, and methine carbons was made on the basis of the ^{1}H off-resonance data, and the chemical shifts of the methylene and methine carbons well conform with those recorded for other η-allylic systems.[13] The central carbon of the η^3-allyl moiety usually resonates at about 100 ppm,[13] but substitution of a proton bonded to a carbon atom with a hydroxy group is known to shift the carbon resonance to 36–51 ppm lower field.[14] Thus the signal at 150.4 ppm may be assigned to C(OH), and then the remaining 212.0 ppm signal may be assigned to C(=O). The signals for CH and COH carbons lie 40–50 ppm upfield on bonding to palladium(II) than those in usual O,O′-chelates.[15] The chemical shift of the carbonyl carbon (212.0 ppm) is a little larger than that (201.7 ppm) reported for the keto tautomer of the acetylacetone molecule[16] in accordance with the proposed hydrogen-bonded structure. The ^{13}C NMR data for **2** are similarly assigned as listed in Table III. The chemical shift of C(=O) is again a little larger than that (166.8 ppm) for the ethoxycarbonyl carbon of the ethyl acetoacetate molecule,[16] conforming to the intramolecular hydrogen bonding.

It is worth noting that acetylacetone and ethyl acetoacetate prefer the η^3 carbon bonding with palladium(II) to the O,-O′-chelation. In fact the reaction of acetylacetone with dichlorobis(benzonitrile)palladium(II) produces **1** ultimately via $[PdCl(acac\text{-}O,O')]_2$ and the η^3 structure is retained in the bridge-splitting reactions with triphenylphosphine, triphenylarsine, and chloride.[1] As is described in the Experimental Section, the reaction of ethyl acetoacetate with palladium(II) chloride in water at 70 °C gave **2** in a high yield, whereas reaction of the ester with sodium tetrachloropalladate(II) in aqueous alkaline solution followed by special workup afforded $Pd(etac\text{-}O,O')_2$.[17] The bridge-splitting reactions of **2** yielded mononuclear complexes **2a**, **2b**, and **2c**. A similar η^3 complex of benzyl acetoacetate [PdCl(benzac-C^1-C^3)py] was also reported.[3] All of these complexes were isolated and gave satisfactory analysis but are not stable in solution, disproportionating according to eq 1. IR spectra of



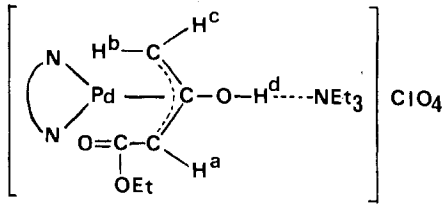
(1)

2a, **2b**, and **2c** in Nujol show very strong ν(C=O) bands in the 1650–1666-cm^{-1} region (Table IV), resembling the 1675-cm^{-1} band of **2**.[2]

Complexes **7a** and **7b** also exhibit the ν(C=O) bands at 1679 and 1667 cm^{-1}, respectively, indicating maintenance of the hydrogen bond. The ^{1}H NMR spectra of **7a** and **7b** resemble the spectrum of **2** except for inversion in the signal positions of H^a and H^c for both complexes and indiscernible coupling of H^d to H^b in **7b**. Complex **7c**, on the other hand, shows different behavior from that of **7a**. Thus the ν(C=O) frequency is 22 cm^{-1} higher than that for **7a**, suggesting breakdown of the hydrogen bond, and a broad band newly appeared at 2670 cm^{-1}. In the ^{1}H NMR spectrum, the 1.5-Hz doublet at 10.93 ppm recorded for **7a** disappeared on addition of triethylamine, and instead **7c** showed a broad singlet at 6.57 ppm, which is assigned to H^d, since it disappeared on addition of D_2O. Signals at 3.72 and 2.68 ppm are assigned to H^c and H^b, respectively. Thus complex **7c** seems to retain the η^3 structure with the enolic hydrogen linked to the amine nitrogen. The IR band at 2670 cm^{-1} may be attributed to the ν(OH) or ν(NH) vibration of the O–H···N moiety.

Table IV. Characteristic IR Data (cm^{-1}) in Nujol

no. of complex	ν(C=O)	ν(C=O)	δ(CCC) or ν(Pd-C)	ν(Pd-Cl)
2a	1666		552	300
2b	1650		548	267, 277
2c	1653		550	270, 280
3a	1723	1630	530	330
3b	1713	1631	531	330
3c	1721	1626	526	330
4a	1730, 1640		543	335
4b	1741, 1638		547	322
4c	1736, 1635		553	330
4d	1730, 1659		553	
5a	1628	1565	538	
5b	1630	1575, 1545	540	
5c	1627	1550	535	
6a	1680	1545, 1525	552	
6b	1677	1572	545	
6c	1670	1550	551	
7a	1679		550	
7b	1667		550	
7c	1701		558	



7c

Terminal-Carbon-Bonded Complexes of the β-Diketonate Monoanions with Palladium(II). Table V shows the ^{1}H NMR data for the terminal-carbon-bonded palladium(II) complexes of monoanions of acetylacetone and ethyl acetoacetate. The ^{1}H NMR spectra of **3b** and **3c** consist of two sets of signals which are assigned to the enol and keto tautomers. In either case the area ratio of two methyl signals gives the equilibrium quotient Q = [enol]/[keto] = 0.7 in chloroform at room temperature. The value practically coincides with that reported for **3a**,[1] indicating that substitution of 2,2′-bipyridine in **3a** with 4,4′-dimethyl-2,2′-bipyridine and 1,10-phenanthroline makes no appreciable difference in the electron-releasing ability of the bis(base)palladium(II) moiety. For complexes **4a–d** no signals assignable to the enol tautomer are observed. The enol content of ethyl acetoacetate itself is much smaller than that of acetylacetone,[18] and palladation at the terminal carbon shifts the equilibrium almost completely to the keto side.

As is seen in Table IV, compounds **4a–d** exhibit two ν-(C=O) bands. The higher frequency one observed in the 1730–1741-cm^{-1} region may be assigned to stretching of the ester carbonyl group and the lower frequency one at the 1635–1659-cm^{-1} region to that of the carbonyl group near the metal. Compounds **3a–c** also show two bands in the ν(C=O) region. The higher frequency band may be ascribed to

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Table V. Proton NMR Chemical Shifts in Ppm from Internal Me_4Si in CD_2Cl_2 for the Terminal-Carbon-Bonded Complexes of β-Diketonate Monoanions with Palladium(II)

no.	complex	form	CH_3	CH_3-CH_2	$Pd-CH_2$	CH_2	OH
3a	[PdCl(acac-C^1)(bpy)]	keto	2.29		2.94	3.96	
		enol	1.95		2.87	6.00[a]	15.47
3b	[PdCl(acac-C^1)(Me_2bpy)]	keto	2.23		2.87	3.90	
		enol	1.92		2.79	5.93[a]	16.03
3c	[PdCl(acac-C^1)(phen)]	keto	2.20		3.07	3.92	
		enol	1.89		3.00	5.98[a]	15.7
4a	[PdCl(etac-C^1)(bpy)]			1.21 4.12	2.91	3.87	
4b	[PdCl(etac-C^1)(Me_2bpy)]			1.28 4.23	2.93	4.09	
4c	[PdCl(etac-C^1)(phen)]			1.20 4.13	3.02	3.90	
4d	[Pd(etac-C^1)(γ-pic)(bpy)]-ClO_4			1.14 4.04	2.80	3.26	

[a] Methine signal for the enol tautomer.

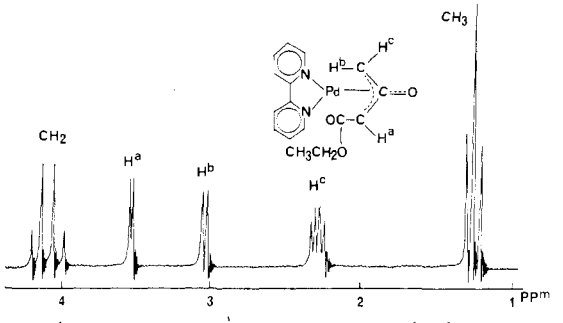

Figure 2. ^1H NMR spectrum of [Pd(etac(2−)-C^1−C^3)(bpy)] (**6a**) in CD_2Cl_2 with internal Me_4Si.

stretching of the carbonyl group far from the metal in the keto tautomer and the lower frequency one to the combined ν(C···O) and ν(C···C···C) vibrations of the enol tautomer. The ν(C=O) band due to the carbonyl group near the metal in the keto tautomer might be overlapped by the enol bands.

η^3 Complexes of the β-Diketonate Dianions with Palladium(II). As Figure 2 shows, the ^1H NMR spectrum of [Pd(etac(2−)-C^1−C^3)(bpy)] (**6a**) is quite simple, consisting of five signals at 1.23 t, 2.27 dd, 3.02 d, 3.53 d, and 4.07 q ppm with the area ratio of 3:1:1:1:2. The triplet at the highest field and the quartet at the lowest field are assigned to the methyl and methylene protons of the ethyl group, respectively. The remaining three signals resemble those for the allylic protons of **2** (Figure 1) in pattern, indicating the maintenance of the η^3-allylic structure. Double doublets at 2.27 ppm, the 4.4-Hz doublet at 3.02 ppm, and the 2.3-Hz doublet at 3.53 ppm are assigned to H^c, H^b, and H^a, respectively. The signal due to the enolic proton is not found in this spectrum, and the anti structure as depicted in Figure 2 is presumed to be favored by **6a** in order to minimize the repulsion between the carbonyl oxygen and the deprotonated enolic oxygen, although the syn structure of **2** was stabilized by the intramolecular hydrogen bonding. The geminal coupling between the end methylene protons is again observed, and the four-bond coupling between two syn protons, H^a and H^c, conforms to the W rule. The syn protons of the anti isomer of η^3-(1-acetyl-2-methallyl)-chloro(pyridine)palladium(II) resonate at 3.93 and 4.72 ppm both as doublets with $^4J(H-H)$ = 1.5 Hz.[12] As compared with these data, chemical shifts of H^c and H^a are more than 1 ppm smaller, and H^b also resonates at more than 1 ppm higher field than the anti proton (4.32 ppm) of the above reference complex. These remarkable upfield shifts of the allylic protons in **6a** seem to be caused by the delocalization of the negative charge on the enolic oxygen through the allylic skelton. Thus the β-diketonate dianion functioning as a η^3 ligand may resemble the trimethylenemethane dianion[19] to some extent.

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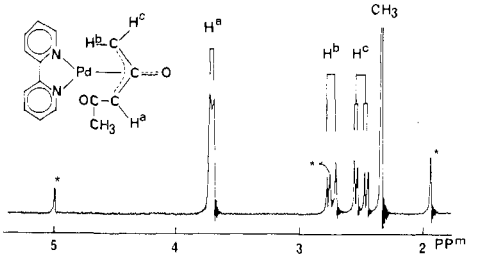


Figure 3. ^1H NMR spectrum of [Pd(acac(2−)-C^1−C^3)(bpy)] (**5a**) in CD_2Cl_2 with internal Me_4Si.

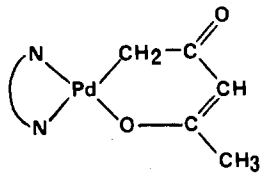
The IR spectrum of **6a** exhibits three maxima in the 1700–1500-cm^{-1} region except the 1600-cm^{-1} band due to the bipyridine ligand. The very strong band at 1680 cm^{-1} is assigned to the stretching of the ester carbonyl group, and the decrease in frequency as compared with that of **2** (1730 cm^{-1}) seems to be caused by the delocalization of the negative charge on the enolic oxygen. The remaining two broad bands at 1545 and 1525 cm^{-1} might be ascribed to the stretching vibrations of the enolic C···O bond.

It should be noted that the methylene protons of the ethyl group in **6a** resonate as a simple quartet, although those in **2** exhibited a 16-line multiplet as was seen in Figure 1. Breakdown of the intramolecular hydrogen bond in **2** by the proton abstraction has caused the free rotation of the ethoxycarbonyl group around the C–C bond, which in turn may have minimized the difference in environments of the diastereotopic methylene protons to the negligibly small. Similar spectral patterns are also observed for compounds **6b** and **6c**.

The ^1H NMR spectrum of **5a** depicted in Figure 3 is quite similar to that of **6a** except for the signals marked with the asterisk and is interpreted reasonably on the basis of the proposed η^3 structure. The H^c double doublets and the H^b doublet are brought close together, although those for compound **6a** are 0.75 ppm apart from each other (Figure 2). A similar situation was also found for the η^3 monoanion complexes. The end methylene protons, H^b and H^c, of [PdCl(acac-C^1−C^3)L] exhibit single resonances at 2.48 ppm (L = PPh_3) and 2.54 ppm (L = $AsPh_3$), and those of **1a** combine with the methyl protons to give rise to a broad 5 H signal at 2.30 ppm,[1] whereas H^b and H^c in the corresponding complexes of ethyl acetoacetate (**2**) and acetoacetic acid[11] resonate about 1 ppm apart from each other.

As is seen in Figure 3 and Table II, three extra singlets denoted by asterisks are observed in the spectrum of **5a**. Their signal positions and area ratio of 3:2:1 strongly indicate that they are assigned to the methyl, methylene, and methine protons successively from the higher field one. The spectra showed no appreciable change at lower (down to −50 °C) and higher (in $CDCl_3$ up to 58 °C) temperatures. Several preparations were similarly contaminated by this byproduct, the content being almost the same (20–25%). Since satisfactory

elemental analysis is obtained for each preparation and the total signal area for the acetylacetonate dianion bears a correct proportion to that for bipyridine (6:8), the byproduct is considered to be an isomer of **5a**. Quite similar situations are encountered in ^{1}H NMR spectra of **5b** and **5c**. Although isolation of this byproduct has not yet been achieved, we tentatively assume structure **8** for it. Recently we have

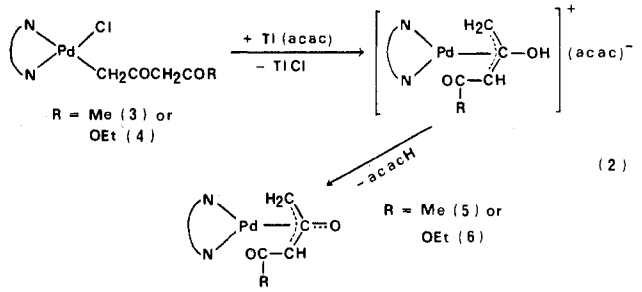


8

prepared the complexes of the trifluoroacetylacetonate dianion with platinum(II), [Pt(tfac(2-)-*C*,*O*)L_2], with triphenylphosphine, tris(*p*-chlorophenyl)phosphine, and triphenylarsine as L, and proposed the C, O-chelate structure for them mainly on the basis of ^{1}H, ^{13}C, ^{19}F, ^{31}P, and ^{195}Pt NMR spectroscopy.[20] The ^{1}H NMR signals for the methylene and methine protons in these complexes appear at 2.78–2.90 and 5.02–5.08 ppm, respectively, the chemical shifts being very close to those for the present byproducts. Compounds **6a–c**, on the other hand, are not contaminated with this kind of byproduct. The C,O-chelate structure may be more unfavorable for ethyl acetoacetate.

The ^{13}C NMR spectrum of **5a** contains five signals assignable to the acetylacetonate dianion. Referring to the ^{1}H off-resonance data and also to the spectrum of **1a**, these signals were easily assigned as is listed in Table III. Compared with the data for **1a**, the central carbon of the allyl moiety resonates at ca. 30 ppm lower field, while the terminal methylene carbon resonates at 7.2 ppm higher field. The former result is readily rationalized since the >C–OH carbon of phenol shows a 13-ppm downfield shift on deprotonation.[21] The increase of shielding on the end methylene carbon might be analogous to the increase of electron density about the β-carbon of ethylene by substitution of hydrogen with an atom carrying unshared electrons.[22] Quite a similar situation is observed for the ^{13}C NMR spectrum of **6b** in comparison with that of **2**, the central carbon of the allylic moiety exhibiting a 27 ppm downfield shift and the terminal methylene carbon a 10 ppm upfield shift.

The η^3 structure of the newly prepared palladium(II) complexes of the β-diketonate dianions has been thus established by means of the ^{1}H and ^{13}C NMR spectroscopy. Preservation of the η^3 structure in **6a** was also demonstrated chemically by isolation of **7a**, **7b**, and an interesting base adduct **7c** and abstraction of the enolic proton in **7a** by the acetylacetonate anion. Similarly the reactions of **3** and **4** with thallium(I) acetylacetonate to afford **5** and **6**, respectively, seem to proceed according to eq 2. Abstraction of a proton from a ligand by



(2)

the acetylacetonate anion in the outer sphere was presumed as an important step in the proton exchange between chloroform and coordinated amine molecules in $[PdL_4](acac)_2$ and $[Pd(acac)L_2](acac)$, where L is primary and secondary amines, respectively.[23]

Each of compounds **5** and **6** still possesses uncoordinated oxygen atoms, suggesting the possibility of coordination with another metal atom. In fact the reaction of **5a** with an equimolar amount of [Pd(hfac)(bpy)](hfac) (hfac = hexafluoroacetylacetonate anion) in dichloromethane at room temperature afforded a yellow precipitate which gave satisfactory analysis as $[Pd_2(acac(2-))(bpy)_2](hfac)_2$. The IR spectrum of this compound shows sharp strong bands at 1668, 1555, 1533, and 1520 cm^{-1}. The 1668-cm^{-1} band is assigned to the uncoordinated hfac anion and the other three bands are characteristic of the O,O′-chelated acetylacetonate ligand. Thus the novel type of bridging of the acetylacetonate dianion is strongly inferred. Unfortunately, however, insolubility of the presumably dinuclear complex in common organic solvents precludes ready characterization. Further investigation on this line is now in progress.

Acknowledgment. We wish to thank Mr. J. Gohda for elemental analyses and Dr. T. Kinoshita for ^{13}C NMR measurements. We are also grateful to the Ministry of Education, Japan, for Grant-in-Aid for Scientific Research (Grant No. 243014).

Registry No. **1**, 65027-69-2; **1a**, 59400-26-9; **2**, 32732-62-0; **2a**, 73193-71-2; **2b**, 73193-73-4; **2c**, 73193-74-5; **3a**, 59588-96-4; **3b**, 73193-75-6; **3c**, 73193-76-7; **4a**, 37821-60-6; **4b**, 73193-77-8; **4c**, 73197-85-0; **4d**, 73197-87-2; **5a**, 70780-91-5; **5b**, 73193-63-2; **5c**, 73193-64-3; **6a**, 70773-29-4; **6b**, 73193-65-4; **6c**, 73193-66-5; **7a**, 70773-31-8; **7b**, 73193-67-6; **7c**, 73193-68-7.

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