Reactions of Bis(acetylacetonato)palladium(II) with Triphenylphosphine and Nitrogen Bases

Shigeru Baba, Tetsuya Ogura, and Shinichi Kawaguchi*
Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi, Osaka 558

(Received November 12, 1973)

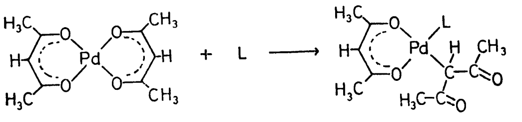
Bis(acetylacetonato)palladium(II) reacts with triphenylphosphine and nitrogen bases such as pyridine, diethylamine, and *N*-methylbenzylamine to transform one of the chelating ligands into the carbon-bonded state. The product complexes of the type Pd(acac)$_2$L have been isolated in high yields and characterized by IR and NMR spectra. Several reactions of Pd(acac)$_2$PPh$_3$ and Pd(acac)$_2$py were also examined.

Acetylacetone is a very versatile ligand showing various modes of bonding to metal atoms.[1] Most usually the acetylacetonate anion coordinates to a metal atom *via* the two oxygen atoms, forming a six-membered chelate ring.[2] The unidentate linkage *via* the central carbon atom is also well known for platinum(II) and other rather soft metal ions,[3] but no example of carbon-bonded palladium(II) complexes of acetylacetone has yet been reported.

The complex K[PtCl(acac)$_2$] was prepared by Werner[4] in 1901 by the reaction of K$_2$[PtCl$_4$] with potassium acetylacetonate in aqueous solution, and was shown by X-ray crystal analysis[5] to have one carbon-bonded and one oxygen-bonded ligands. On the other hand, similar reactions of K$_2$[PdCl$_4$] with acetylacetonate anions under various conditions produce only the simple chelate Pd(acac)$_2$.[3] However, in our study of the reaction between Pd(acac)$_2$ and triphenylphosphine in benzene to prepare Pd(PPh$_3$)$_4$, the carbon-bonded acetylacetonate complex Pd(acac)$_2$(PPh$_3$) was obtained as a stable intermediary product.[6] This paper reports the preparation and characterization of several palladium(II) complexes containing the carbon-bonded acetylacetonate ligand.

Results and Discussion

Preparation. Bis(acetylacetonato)palladium(II), Pd(acac)$_2$, reacts with excess triphenylphosphine in benzene at room temperature to produce Pd(PPh$_3$)$_4$ or PdO$_2$(PPh$_3$)$_2$ in the absence or presence of oxygen, respectively. However, an equimolar amount of triphenylphosphine gave a carbon-bonded acetylacetonate complex, Pd(acac)$_2$(PPh$_3$) [**1a**], in a high yield. Nitrogen bases such as pyridine, diethylamine, and *N*-methylbenzylamine also reacted with Pd(acac)$_2$ to transform one of the chelating ligands into the carbon-bonded state (Eq. (1)). The analytical data of the products are summarized in Table 1.



(1)

L=PPh$_3$[**1a**], Py[**1b**], NHEt$_2$[**1c**],
or NH(Me)CH$_2$Ph[**1d**]

Triphenylarsine and benzonitrile did not react with Pd(acac)$_2$. Either twice as many moles of triphenylphosphine or excess nitrogen bases did not afford the palladium(II) complex containing two carbon-bonded acetylacetonate ligands, but resulted in the compounds **1** alone. The bidentate bases such as 1,2-bisdiphenylphosphinoethane, 2,2′-bipyridine, 1,10-phenanthroline, ethylenediamine, and *N*,*N*′-dimethylethylenediamine did not produce the aimed compounds, either. It is not yet clear why the palladium(II) complex containing two carbon-bonded acetylacetonate ligand can not be obtained, but the existence of one acetylacetonate chelate ring might be necessary to stabilize the carbon-bonding of the other acetylacetonate ligand.

Infrared and NMR Spectra. The characteristic stretching vibrations in the carbon-bonded acetylacetonate complexes are summarized in Table 2. The ν(C=O) and ν(C=C) bands of the chelating acetylacetonate ligand appear in the 1500—1600 cm^{-1} region, and the absorption bands in the 1600—1700 cm^{-1} region which are not observed for Pd(acac)$_2$ can be unequivocally assigned to the ν(C=O) vibrations of the carbon-bonded acetylacetonate ligand.[7] The strong band which is observed in the 500—550 cm^{-1} region

Table 1. Analytical data of palladium(II) complexes

Complex	Found %			Calcd %			Mol. wt. Found (Calcd)	Color	Dec. pt. °C
	C	H	N	C	H	N			
Pd(acac)$_2$PPh$_3$	59.38	5.77		59.32	5.16		560 (567)	yellow-orange	142
Pd(acac)$_2$py	46.92	5.06	3.92	46.95	4.99	3.65	381 (383)	yellow-green	150
Pd(acac)$_2$NHEt$_2$	44.20	6.84	4.27	44.51	6.67	3.71	380 (377)	yellow	106
Pd(acac)NH(Me)CH$_2$Ph	51.93	6.04	3.74	52.12	5.75	3.20	410 (437)	yellow	156
PdCl(acac)PPh$_3$	55.60	4.79		54.90	4.40		500 (503)	orange	162
PdCl(acac)py	37.53	3.76	4.79	37.52	3.78	4.40	302 (320)	reddish orange	160
PdOCOCH$_3$(acac)PPh$_3$	56.75	5.19		56.99	4.78		510 (527)	yellow	135
PdOCOCH$_3$(acac)py	42.01	4.78	4.04	42.31	4.44	4.11	340 (310)	orange	117

---

* Correspondences should be addressed to this author.

TABLE 2. INFRARED SPECTRA IN NUJOL MULL (cm^{-1})[a]

Complex	C-bonded acac ν(C=O)	ν(Pd–C)	O-bonded acac ν(C=O)+ν(C=C)	ν(Pd–Cl)	CH$_3$COO ν(C=O)
Pd(acac)$_2$PPh$_3$	1665 vs 1632 s	540 vs	1572 vs, 1550 s 1523 vs		
Pd(acac)$_2$py	1680 vs 1640 m	524 vs	1568 vs, 1548 m, sh 1521 vs		
Pd(acac)$_2$NHEt$_2$	1675 vs 1630 m	519 vs	1575 vs, 1562 s, sh 1521 vs		
Pd(acac)$_2$NH(Me)CH$_2$Ph	1678 vs 1630 m	518 s	1570 vs, 1558 s 1521 s		
PdCl(acac)PPh$_3$			1568 s, 1545 m, sh 1521 vs	360 s	
PdCl(acac)py			1567 s, 1558 m, sh 1520 vs	348 vs	
PdOCOCH$_3$(acac)PPh$_3$			1578 vs, 1558 m, sh 1515 s		1640 vs
PdOCOCH$_3$(acac)py			1561 s, 1550 m, sh 1520 vs		1632 vs

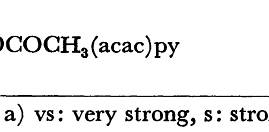
a) vs: very strong, s: strong, m: medium, sh: shoulder

can be attributed to the ν(Pd–C) vibration.

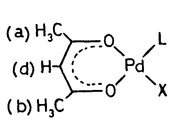
The coexistence of one oxygen-chelating and one carbon-bonded acetylacetonate ligands in the complexes **1a**—**1d** is clearly revealed by the proton NMR spectra listed in Table 3. The NMR spectra of platinum(II) complexes containing the carbon-bonded acetylacetonate ligand have been studied extensively by Lewis and his co-workers,[8] and are referred to here in assigning the present spectra.

In a spectrum of Pd(acac)$_2$PPh$_3$ [**1a**] three methyl-proton signals are observed each as a singlet at 8.46, 7.96, and 7.86 τ with the intensity ratio of 1 : 1 : 2. The lowest-field peak is assigned to the two methyl groups of the carbon-bonded acetylacetonate ligand, indicating that the two methyl groups are equivalent on account of free rotation of the ligand around the Pd–C bond. The two peaks of equal intensity at 8.46 and 7.96 τ are attributed to the two methyl groups of the chelating acetylacetonate ligand. As is noticed in Table 3, the highest-field signal is shifted appreciably when triphenylphosphine is replaced by other ligands, while the lower-field one is not sensitive to the nature of L. Such an anisotropic shielding effect of the triphenylphosphine ligand is expected to be experienced by the methyl group nearer to this ligand, and thus the highest-field signal is assigned to the acetylacetonate-methyl group in the *cis* position of L. Similar situations have also been found for PtCl(acac)L complexes containing various tertiary phosphines and other bases as L.[8,9]

TABLE 3. NMR DATA RECORDED AT 60 MHz IN CDCl$_3$ (τ Values relative to internal TMS)[a]



L	O-Bonded acac ligand CH$_3$(a)	CH$_3$(b)	CH(d)	C-Bonded acac ligand CH$_3$(c)	CH(e)
PPh$_3$	8.46	7.96	4.70	7.86	6.46[b]
py	8.10	8.00	4.66	7.86	5.76
NH(Me)CH$_2$Ph	8.03	7.99	4.63	7.80	5.50



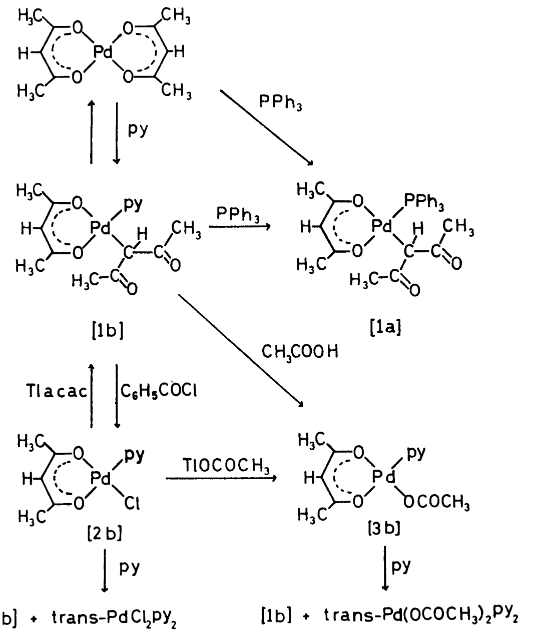
L	X	CH$_3$(a)	CH$_3$(b)	CH(d)	CH$_3$COO
PPh$_3$	Cl	8.46	7.93	4.70	
py	Cl	7.96	7.90	4.53	
PPh$_3$	OCOCH$_3$	8.36	7.96	4.66	8.50
py	OCOCH$_3$	8.06	8.00	4.63	8.00

a) All signals except the following one are singlets.
b) Doublet, J_{P-H}=6.3 Hz.

It has been well established for the platinum(II) complexes[10] that the methine proton of the carbon-bonded acetylacetone absorbs at higher field in comparison with that of the chelating acetylacetone. This assignment holds also for the palladium(II) complexes, and the methine proton signal of the carbon-bonded acetylacetone in the phosphine complex **1a** appears as a doublet because of coupling with the phosphorus nucleus (J_{P-H}=6.3 Hz).

Reactions of Pd(acac)$_2$L. The compound **1a** reacts with more than three mole equivalents of triphenylphosphine to produce tetrakis(triphenylphosphine)palladium(0). Benzoyl chloride reacts with **1a** in benzene at room temperature to replace the carbon-bonded acetylacetonate ligand with a chloride anion, affording PdCl(acac)PPh$_3$ [**2a**]. The loss of the carbon-bonded acetylacetone is clearly evidenced by the IR and NMR spectra (Tables 2 and 3). The compound **2a** can be transformed again to **1a** by the reaction with thallium(I) acetylacetonate. **2a** also reacts with thallium(I) acetate to form Pd(OCOCH$_3$)(acac)PPh$_3$ [**3a**], which can alternatively derived from **1a** by the direct reaction with acetic acid. It should be noted that Pd(acac)$_2$ does not react with acetic acid, but the carbon-bonded acetylacetonate group in **1a** can be easily displaced by the reaction with acetic acid.

The mechanism of the reaction of **1a** with acetic acid or benzoyl chloride is not clear at the present stage of investigation, but the oxidative addition of the reactant to **1a** might have occurred, being followed by the reductive elimination of acetylacetone or its benzoyl derivative.



Scheme

As is summarized in the Scheme, similar reactions are also observed for the compound **1b** to produce PdCl(acac)py [**2b**] and PdOCOCH$_3$(acac)py [**3b**]. The compound **1b** was prepared by the reaction of Pd(acac)$_2$ with pyridine, but the reaction can be reversed. When **1b** was dissolved in benzene, refluxed for about one hour, and the solvent was distilled off under reduced pressure, Pd(acac)$_2$ was recovered. The ligand pyridine can also be replaced by triphenylphosphine to give **1a**.

It is very interesting that the compound **2b** reacts with pyridine to produce *trans*-PdCl$_2$py$_2$ and Pd(acac)$_2$py [**1b**]. These products correspond to the disproportionation of **2b** to form PdCl$_2$py$_2$ and Pd(acac)$_2$ followed by the reaction of Pd(acac)$_2$ with pyridine to give **1b**. However such a disproportionation reaction of **2b** does not occur spontaneously, but needs pyridine as a trigger reagent. The acetate complex **3b** also reacts with pyridine to afford *trans*-Pd(OCOCH$_3$)$_2$py$_2$ and **1b**.

The mechanism of this kind of interesting reaction is not yet clear, but the reaction proceeds quite readily and offers a useful and convenient route for the synthesis of *trans*-Pd(OCOCH$_3$)$_2$py$_2$. Bis(acetylacetonato)palladium(II) readily reacts with pyridine and acetic acid in benzene at room temperature to form *trans*-Pd(OCOCH$_3$)$_2$py$_2$ in a high yield.

Experimental

Reactions of Pd(acac)$_2$ with Bases. A mixture of Pd(acac)$_2$ (0.272 g, 0.89 mmol) and PPh$_3$ (0.240 g, 0.91 mmol) was stirred in benzene (6 ml) at room temperature until the solution became transparent. Then petroleum ether (bp 30—60 °C) was added to separate the product. Yield 0.473 g, 87%. Yellow-orange crystals of Pd(acac)$_2$PPh$_3$·$\frac{1}{2}$C$_6$H$_6$ were obtained by recrystallization from benzene–petroleum ether, but those recrystallized from chloroform did not involve the lattice solvent.

A mixture of Pd(acac)$_2$ (0.290 g, 0.95 mmol) and pyridine (5 ml) was warmed at about 80 °C until a clear solution resulted. Petroleum ether was added to precipitate Pd(acac)$_2$py. Yield 0.332 g, 91%. Yellow-green crystals were obtained by recrystallization from benzene–petroleum ether. Pd(acac)$_2$NH(Me)CH$_2$Ph was also prepared by a similar reaction in a yield of 90%.

A mixture of Pd(acac)$_2$ (0.353 g, 1.15 mmol) and NHEt$_2$ (5 ml) was stirred at room temperature until a clear solution was obtained. Then the amine was evaporated spontaneously to leave the product Pd(acac)$_2$NHEt$_2$, which was recrystallized from cyclohexane. Yield 0.39 g, 87%.

The Reaction of Pd(acac)$_2$PPh$_3$ with Excess Triphenylphosphine. The complex Pd(acac)$_2$PPh$_3$ (0.202 g, 0.35 mmol) was allowed to react with triphenylphosphine (0.380 g, 1.45 mmol) in benzene at room temperature in an atmosphere of nitrogen. Petroleum ether was added to the dark red solution to separate out the product Pd(PPh$_3$)$_4$. Yield 0.335 g, 81%.

The Reactions of Pd(acac)$_2$PPh$_3$ and Pd(acac)$_2$py with Benzoyl Chloride. A mixture of Pd(acac)$_2$PPh$_3$ (0.205 g, 0.35 mmol) and benzoyl chloride (2 ml) was stirred in benzene (5 ml) at room temperature until a reddish orange solution resulted. Petroleum ether was then added to precipitate the product PdCl(acac)PPh$_3$. Yield 0.172 g, 95%. Reddish orange crystals were obtained by recrystallization from benzene–petroleum ether. Orange crystals of PdCl(acac)py were similarly prepared in a yield of 85%.

The Reactions of PdCl(acac)PPh$_3$ and PdCl(acac)py with Thallium(I) Acetylacetonate. Thallium(I) acetylacetonate (0.015 g, 0.05 mmol) was added to a solution of PdCl(acac)PPh$_3$ (0.024 g, 0.05 mmol) in chloroform (10 ml) and the mixture was stirred at room temperature for 30 min. Thallium(I) chloride was filtered off and the filtrate was concentrated by evaporation under reduced pressure to separate out Pd(acac)$_2$PPh$_3$. Yield 0.024 g, 88%. Pd(acac)$_2$py was also derived from PdCl(acac)py by a similar procedure in a yield of 90%.

Reactions of Pd(acac)$_2$py to Pd(acac)$_2$ and Pd(acac)$_2$PPh$_3$. A solution of Pd(acac)$_2$py in benzene was refluxed for 1 hr and the solvent was distilled off. Pd(acac)$_2$ was recovered. In another experiment, triphenylphosphine (0.300 g, 0.12 mmol) was added to a solution of Pd(acac)$_2$py (0.348 g, 0.11 mmol) in benzene. After stirring for 10 min, the solution was concentrated to separate out Pd(acac)$_2$PPh$_3$. Yield 0.500 g, 90%.

Preparations of PdOCOCH$_3$(acac)PPh$_3$ and PdOCOCH$_3$(acac)py. To a solution of PdCl(acac)PPh$_3$ (0.162 g, 0.32 mmol) in methylene chloride (10 ml) was added thallium(I) acetate (0.102 g, 0.39 mmol), and the mixture was stirred for 30 min at room temperature. Thallium(I) chloride was filtered off, and the filtrate was concentrated by evaporation under reduced pressure to separate out PdOCOCH$_3$(acac)PPh$_3$. Yield 0.167 g, 97%.

The corresponding pyridine complex PdOCOCH$_3$(acac)py was similarly prepared from PdCl(acac)py in a yield of 86%. The acetate complex was also prepared by the direct reaction of Pd(acac)$_2$py (0.167 g, 0.04 mmol) with acetic acid (2 ml) in benzene. The solution was stirred for 3 hr at room temperature. After the evaporation of benzene and acetic acid under reduced pressure, the residue was recrystallized from benzene–petroleum ether. Yield 0.125 g, 84%.

The Reactions of PdCl(acac)py and PdOCOCH$_3$(acac)py with pyridine. Pyridine (2 ml) was added to a solution of PdCl(acac)py (0.114 g, 0.36 mmol) in benzene (10 ml). The reaction occurred rapidly to precipitate *trans*-PdCl$_2$py$_2$ (yield 0.054 g, 44% on the basis of palladium). Petroleum ether was added to the concentrate of the filtrate to separate out Pd(acac)$_2$py (yield 0.067 g, 48%).

Pyridine (2 ml) was added to a solution of PdOCOCH$_3$(acac)py (0.139 g, 0.41 mmol) in benzene (10 ml). After stirring for 3 hr at room temperature the solution was concentrated to yield precipitates. Concentration to separate out precipitate was repeated further twice. Resultant yield of *trans*-Pd(OCOCH$_3$)$_2$py$_2$·H$_2$O was 0.075 g, 46%. From the final filtrate Pd(acac)$_2$py was obtained in a yield of 0.059 g, 38%.

Preparation of trans-*Pd(OCOCH$_3$)$_2$py$_2$ from Pd(acac)$_2$.* When pyridine (2 ml) and acetic acid (2 ml) were added to a suspension of Pd(acac)$_2$ (0.241 g, 0.79 mmol) in benzene (12 ml), the mixture became transparent immediately and changed its color from red to pale yellow. After stirring for 20 min petroleum ether was added to the solution to yield *trans*-Pd(OCOCH$_3$)$_2$py$_2$. Yield 0.300 g, 94%. White needles were obtained by the recrystallization from methylene chloride–petroleum ether. Found: C, 42.00; H, 4.63; N, 7.08%. Calcd for Pd(OCOCH$_3$)$_2$py$_2$·H$_2$O: C, 41.96; H, 4.52; N, 6.99%. The ν(C=O) absorption is observed at 1600 cm^{-1}, and the CH$_3$-proton signal at 8.16 τ.

Measurements. Infrared absorption spectra in the 4000—600 cm^{-1} region were measured with a JASCO IR-E spectrophotometer and those in the 700—200 cm^{-1} region with a Hitachi grating infrared spectrophotometer EPI-L. The NMR spectra were recorded at 60 MHz with tetramethylsilane as the internal reference on a C-60 HL spectrometer of Japan Electron Optics. The molecular weight was determined in dichloromethane at 25 °C by the method of vapor pressure osmometry with an apparatus manufactured by Knauer, Germany.

We are indebted to Mr. J. Gohda and Miss M. Iwao for the elemental analyses and NMR measurements. Financial aid by the Ministry of Education and the kind supply of acetylacetone by the Daicel Co., Ltd. are also acknowledged.

References

1) D. W. Thompson, *Structure and Bonding*, **9**, 27 (1971); B. Bock, K. Flatau, H. Junge, M. Kuhr, and H. Musso, *Angew. Chem.*, **83**, 239 (1971).

2) J. P. Fackler, Jr., *Progress Inorg. Chem.*, **7**, 361 (1966).

3) D. Gibson, *Coord. Chem. Rev.*, **4**, 225 (1969).

4) A. Werner, *Ber.*, **34**, 2584 (1901).

5) R. Mason, G. B. Robertson, and P. J. Pauling, *J. Chem. Soc. (A)*, **1969**, 485.

6) A short communication appeared in S. Baba, T. Ogura, and S. Kawaguchi, *Inorg. Nucl. Chem. Lett.*, **7**, 1195 (1971).

7) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd. ed., Wiley–Interscience, New York (1970), pp. 247—256.

8) G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., (A)*, **1970**, 1732 and references cited therein.

9) C. E. Holloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *ibid.*, **1970**, 1653.

10) J. Lewis, R. F. Long, and C. Oldham, *J. Chem. Soc.*, **1965**, 6740.