

Syntheses of Six-membered Cyclopalladated Complexes of 2-Benzoylpyridine

Yoshio FUCHITA, Katsuma HIRAKI,* and Yasunori KAGE

Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Bunkyo-machi, Nagasaki 852

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Synopsis. 2-Benzoylpyridine reacts with $\text{Pd}(\text{OAc})_2$ to give a new six-membered cyclopalladated complex, $[\{\text{Pd}(\text{pcph})(\text{OAc})\}_2] \cdot 0.25\text{CH}_2\text{Cl}_2$ [$\text{pcph} = 2-(2\text{-pyridylcarbonyl})\text{phenyl-}C^1, N$] (**1**). A chloro-bridged analogue, $[\{\text{Pd}(\text{pcph})\text{Cl}\}_2]$, prepared by the metathetical reaction of **1** with LiCl , undergoes bridge-splitting reactions with 3,5-lutidine and $\text{Tl}(\text{acac})$ to yield the corresponding mononuclear cyclopalladated complexes.

Many studies have been reported on the five-membered cyclopalladated complexes of aryl-substituted nitrogen bases.^{1,2} However, as concerns six-membered cyclopalladated complexes having nitrogen donor atoms, only two reports have appeared on N, N' -diarylamidines³ and N, N -diethyl-3-phenylthiomethoxy-4-methoxyphenethylamine.⁴ Recently, it was found in our laboratory that 2-benzoylpyridine readily produces a six-membered cyclopalladated complex by the reaction with palladium(II) acetate.⁵ In continuation of our studies about the six-membered cyclopalladated complexes, we wish to report on the cyclopalladation of 2-benzoylpyridine (bzopy) by palladium(II) acetate resulting in the formation of $[\{\text{Pd}(\text{pcph})(\text{OAc})\}_2]$ (**1**) [$\text{pcph} = 2-(2\text{-pyridylcarbonyl})\text{phenyl-}C^1, N$].

Experimental

All the new complexes synthesized in this study were characterized in the same way as described in an earlier paper.⁶ Molecular weights were determined in benzene with a Corona Model 114 molecular weight apparatus at 41.7°C.

Preparation of $[\{\text{Pd}(\text{pcph})(\text{OAc})\}_2] \cdot 0.25\text{CH}_2\text{Cl}_2$ (**1**).

An acetic acid suspension (20 ml) containing palladium(II) acetate (3.1 mmol) and bzopy (3.7 mmol) was refluxed for 1.5 h, and then filtered, to give a yellow cake and a yellow solution. The yellow cake was successively washed well with water and a small amount of methanol, and recrystallized from dichloromethane/hexane to give 0.56 g of **1** as yellow crystals. An additional amount (0.28 g) of **1** was obtained as yellow precipitates from the yellow solution after extraction of it with dichloromethane, concentration of the extract, and dilution with hexane. Yield 76%; mp 240–243°C (dec); MW 705.4 (Calcd 716.6).

Preparation of $[\{\text{Pd}(\text{pcph})\text{Cl}\}_2]$ (2**).** A THF–water (120 ml/10 ml) suspension containing **1** (1.2 mmol) and LiCl

(7.5 mmol) was stirred for 12 h. The precipitated yellow solid was filtered, and washed with a methanol/water (20 ml/20 ml) mixture to give **2**. Yield 95%; mp > 300°C.

Reaction of **2 with 3,5-Lutidine.** A dichloromethane solution (10 ml) containing **2** (0.23 mmol) and 3,5-lutidine (lut) (0.51 mmol) was stirred at room temperature for 5 h. Addition of hexane to the resulting mixture gave $[\text{Pd}(\text{pcph})\text{Cl}(\text{lut})] \cdot 0.1\text{CH}_2\text{Cl}_2$ (**3**) as pale yellow crystals. Yield 79%; mp > 300°C.

Reaction of **2 with $\text{Tl}(\text{acac})$.** A dichloromethane suspension (15 ml) of **2** (0.46 mmol) and thallium(I) acetylacetonate (0.95 mmol) was stirred at room temperature for 1 d. After centrifuging the resulting milky suspension, the supernatant solution was passed through a silica-gel column (200 mesh, $20\phi \times 140$ mm) with dichloromethane as an eluent. A pale yellow fraction was collected and concentrated. Addition of hexane gave $[\text{Pd}(\text{pcph})(\text{acac})]$ (**4**) as yellow crystals. Yield 39%; mp 229–230°C (dec).

Results and Discussion

2-Benzoylpyridine reacted with palladium(II) chloride in refluxing ethanol to afford only an addition complex, bis(2-benzoylpyridine)dichloropalladium(II), giving no cyclopalladated complex. However, bzopy reacted readily with palladium(II) acetate in refluxing acetic acid to produce a new six-membered cyclopalladated complex **1** in a high yield. It is noteworthy that bzopy, which contains an electron-attracting carbonyl group, undergoes easily cyclopalladation reaction with palladium(II) acetate, in contrast with the results of the earlier studies concerning the electronic effect on the cyclopalladation reaction of substituted azobenzenes.^{7,8} Complex **1** was treated with LiCl to give **2**, which reacted with lut and $\text{Tl}(\text{acac})$ to afford the corresponding mononuclear cyclopalladated complexes, **3** and **4**, respectively (Scheme 1). All the new complexes prepared in this study show considerably high thermal stability. The IR spectra of **1**–**4** showed bands at ca. 1670 cm^{-1} due to a $\nu(\text{C}=\text{O})$ vibration in pcph moiety. This band did not shift virtually in comparison with that in free bzopy (1670 cm^{-1}).

The IR spectrum of **1** showed two characteristic bridging acetato bands⁹ at 1585 and 1430 cm^{-1} . This

TABLE 1. ELEMENTAL ANALYSES AND ^1H NMR DATA OF THE PALLADIUM(II) COMPLEXES

Compd	Found (Calcd) (%)			^1H NMR (δ)		
	C	H	N	6'-H	Me	Others
1	47.15 (47.35)	3.19 (3.16)	3.66 (3.91)	8.25 d ^b	2.05 s	5.28 s (CH_2Cl_2)
2	44.30 (44.47)	2.58 (2.49)	4.22 (4.32)	— ^c	— ^c	— ^c
3	51.75 (52.17)	3.97 (3.94)	6.27 (6.37)	9.52 dd ^{b, d}	2.28 s	7.39 s (H^1) 8.29 s (H^2) 5.28 s (CH_2Cl_2)
4	52.38 (52.66)	3.91 (3.90)	3.56 (3.61)	9.08 dd ^{b, d}	2.01 s 2.06 s	5.04 s (CH)

a) In CDCl_3 . See the text about the aromatic protons. d=Doublet, dd=double doublet, and s=singlet. b) $^3J_{\text{HH}} = 7$ Hz. c) Not recorded owing to its poor solubility. d) $^4J_{\text{HH}} = 2$ Hz.

complex did not show temperature-dependent ^1H NMR spectra in the range of 57 — 50°C , indicating that the six-membered pcph-palladium ring is virtually planar; if this ring were nonplanar and had a boat conformation, temperature-dependent ^1H NMR spectra attributable to an inversion of the ring would be observed as was seen in the palladated 2-(2-picoly)-phenyl- C^1,N ring.⁵⁾ The ^1H NMR spectrum of **1** exhibited one sharp singlet due to the μ -acetato-methyl protons at δ 2.05, indicating that **1** has only one ($a-C^1,b-N$)($g-N,h-C^1$) typed isomer¹⁰⁾ (Scheme 1).

In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** in CDCl_3 , three aromatic quaternary carbon signals at δ 132.6, 143.2, and 150.5 were ascribed to 2-C, 1-C, and 2'-C, respectively, by comparison with the data of acetophenone (1-C, δ 137.1),¹¹⁾ a cyclopalladated complex (1-C, δ 143.3),⁵⁾ and 2-acetylpyridine (2-C, δ 154.1).¹²⁾ These data confirm strongly a cyclopalladated structure of the pcph moiety in **1**. Other eight aromatic tertiary carbon signals appeared as singlets at δ 124.6, 125.4, 126.6, 128.5, 130.4, 134.0, 138.6, and 151.6. Only the last signal (δ 151.6) was assigned to 6'-C (6-C of 2-acetylpyridine, δ 149.5).¹²⁾ Two lower field singlets at δ 181.3 and 190.3 were ascribed to μ -acetato-carboxylato carbon [$\text{Mo}_2(\mu\text{-O}_2\text{CMe})(\text{Ph})_3(\text{PMe}_3)_3$, δ 182.7]¹³⁾ and carbonyl one, respectively. The μ -acetato-methyl carbon signal also appeared as a singlet at δ 24.5.

Complex **2** was assigned to a chloro-bridged binuclear complex on the basis of the elemental analysis and the characterization of the derivatives from **2** as stated below.

In the ^1H NMR spectrum of **3**, eight aromatic protons of the pcph moiety appeared as two sets of well-separated ABCD pattern (Fig. 1). In consideration of the magnetic anisotropy due to the lutidine ring^{5,6)} and the original chemical shifts of free bzopy,¹⁴⁾ four double doublets at δ 6.69, 7.75, 8.14, and 9.52 were assigned to H^6 , $\text{H}^{3'}$, H^3 , and $\text{H}^{6'}$, respectively, and four double triplets at δ 6.98, 7.12, 7.49, and 7.95 were ascribed to H^5 , H^4 , $\text{H}^{5'}$, and $\text{H}^{4'}$, respectively. The coupling constants were $^3J_{\text{HH}}=7$ Hz and

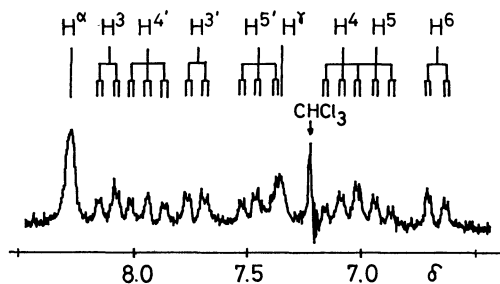


Fig. 1. Low field region of the ^1H NMR spectrum of **3**.

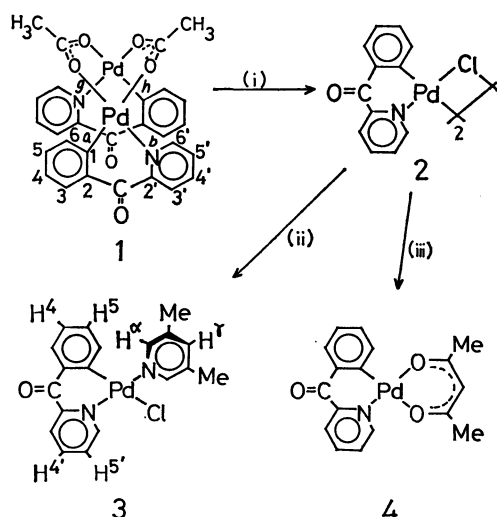
$^4J_{\text{HH}}=2$ Hz.

The IR spectrum of **4** exhibited two strong bands at 1590 and 1515 cm^{-1} , characteristic of the O,O' -chelating acetylacetonato ligand. This complex also showed two sets of relatively clear ABCD pattern, which consisted of two doublets at δ 7.72 and 7.78, two double doublets at δ 8.82 and 9.08 ($\text{H}^{6'}$) [$^3J_{\text{HH}}=ca. 7$ Hz, $^4J_{\text{HH}}=ca. 2$ Hz], two triplets at δ 7.13 and 7.27, and two double triplets at δ 7.51 and 7.98. The mass spectrum exhibited the parent ion peak at m/e 387, together with the fragment ion peak at m/e 288 [$(\text{P}-\text{acac})^+$].

Styrene reacted with **2** in the presence of tripropylamine in refluxing m -xylene for 30 h to give a brownish black oil. After column chromatographic treatment on alumina, this oil was proved to contain both bzopy and *trans*-2-(2-pyridylcarbonyl)stilbene (**5**) in about 68 and 25% yields, respectively. The formation of **5** was confirmed by the ^1H NMR spectrum of the oil in CCl_4 [δ 6.82 d ($^3J_{\text{HH}}=16$ Hz, 1H, olefinic proton)] and its mass spectrum [m/e 285 (P^+)], supporting the cyclopalladated structure in **2**. However, the separation of these two compounds has not been achieved even after repeated column chromatographic treatments.

References

- 1) M. I. Bruce, *Angew. Chem., Int. Ed. Engl.*, **16**, 73 (1977).
- 2) I. Omae, *Chem. Rev.*, **79**, 287 (1979).
- 3) N. D. Cameron and M. Kilner, *J. Chem. Soc., Chem. Commun.*, **1975**, 687.
- 4) R. A. Holton and R. V. Nelson, *J. Organomet. Chem.*, **201**, C35 (1980).
- 5) K. Hiraki, Y. Fuchita, and K. Takechi, *Inorg. Chem.*, **20**, 4316 (1981).
- 6) Y. Fuchita, K. Hiraki, T. Yamaguchi, and T. Maruta, *J. Chem. Soc., Dalton Trans.*, **1981**, 2405.
- 7) H. Takahashi and J. Tsuji, *J. Organomet. Chem.*, **10**, 511 (1967).
- 8) M. I. Bruce, B. L. Goodall, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, **1978**, 687.
- 9) H. Onoue and I. Moritani, *J. Organomet. Chem.*, **43**, 431 (1972).
- 10) K. Hiraki, Y. Fuchita, H. Nakaya, and S. Takakura, *Bull. Chem. Soc. Jpn.*, **52**, 2531 (1979).
- 11) L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra," John Wiley & Sons, New York (1972).
- 12) G. Miyajima, Y. Sasaki, and M. Suzuki, *Chem. Pharm. Bull.*, **20**, 429 (1972).
- 13) R. A. Jones and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, **1979**, 472.
- 14) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).



Scheme 1. (i) LiCl . (ii) 3,5-Lutidine. (iii) $\text{Ti}(\text{acac})_3$.