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Syntheses of Six-membered Cyclopalladated Complexes of 2-Benzoylpyridine

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Synopsis. 2-Benzoylpyridine reacts with Pd(OAc)$_2$ to give a new six-membered cyclopalladated complex, [{Pd(pcph)(OAc)}$_2$]·0.25CH$_2$Cl$_2$ [pcph=2-(2-pyridylcarbonyl)phenyl-C^1,N] (**1**). A chloro-bridged analogue, [{Pd(pcph)Cl}$_2$], prepared by the metathetical reaction of **1** with LiCl, undergoes bridge-splitting reactions with 3,5-lutidine and Tl(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'-diarylamidines[3] and N,N-diethyl-3-phenylthiomethoxy-4-methoxyphenethylamine.[4] Recently, it was found in our laboratory that 2-benzylpyridine 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 [{Pd(pcph)(OAc)}$_2$] (**1**) [pcph=2-(2-pyridylcarbonyl)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 [{*Pd(pcph)(OAc)*}$_2$]·*0.25CH$_2$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 [{*Pd(pcph)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 [Pd(pcph)Cl(lut)]·0.1CH$_2$Cl$_2$ (**3**) as pale yellow crystals. Yield 79%; mp>300 °C.

Reaction of 2 with Tl(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, 20ϕ × 140 mm) with dichloromethane as an eluent. A pale yellow fraction was collected and concentrated. Addition of hexane gave [Pd(pcph)(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 Tl(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 ν(C=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 bands[9] at 1585 and 1430 cm^{-1}. This

Table 1. Elemental analyses and ^{1}H NMR data of the palladium(II) complexes

Compd	Found (Calcd) (%)			^{1}H 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$_2$Cl$_2$)		
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$^\gamma$)	8.29 s(H$^\alpha$)	5.28 s(CH$_2$Cl$_2$)
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) $^3J_{HH}$=7 Hz. c) Not recorded owing to its poor solubility. d) $^4J_{HH}$=2 Hz.

complex did not show temperature-dependent ^{1}H 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 ^{1}H NMR spectra attributable to an inversion of the ring would be observed as was seen in the palladated 2-(2-picolyl)-phenyl-C^1,N ring.[5] The ^{1}H 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 isomer[10] (Scheme 1).

In the ^{13}C{^{1}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 [Mo$_2$(μ-O$_2\underline{\mathrm{C}}$Me)(Ph)$_3$(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 ^{1}H 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, H$^{3'}$, H^3, and 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, H$^{5'}$, and H$^{4'}$, respectively. The coupling constants were $^3J_{\mathrm{HH}}=7$ Hz and $^4J_{\mathrm{HH}}=2$ Hz.

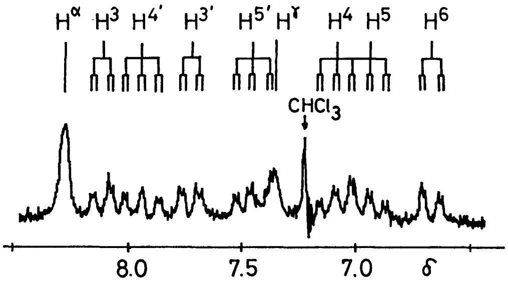
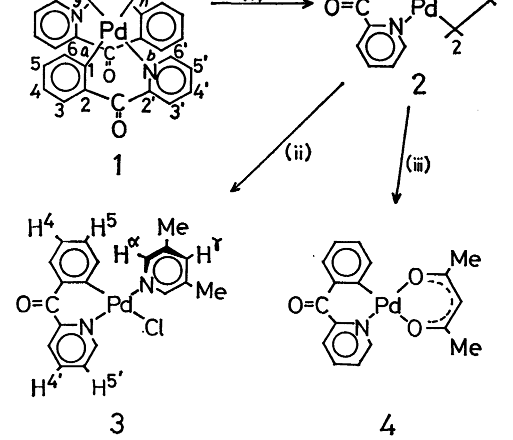


Fig. 1. Low field region of the ^{1}H NMR spectrum of **3**.

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 (H$^{6'}$) [$^3J_{\mathrm{HH}}=$ *ca.* 7 Hz, $^4J_{\mathrm{HH}}=$*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 [(P$-$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 ^{1}H NMR spectrum of the oil in CCl$_4$ [δ 6.82 d ($^3J_{\mathrm{HH}}=16$ 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.



Scheme 1. (i) LiCl. (ii) 3,5-Lutidine. (iii) Tl(acac).

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