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Metallation of aliphatic carbon atoms

VI *. Reactions of 2-pivaloylpyridine with palladium(II) acetate resulting in cyclopalladation and nucleophilic attacks on carbonyl carbon **

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Abstract

The reaction of 2-pivaloylpyridine and palladium(II) acetate in acetic acid at 90–95 °C gives a binuclear, six-membered cyclopalladated complex, $[\{Pd[CH_2CMe_2C(=O)C_5H_4N](\mu\text{-}MeCO_2)\}_2]$. Treatment of this complex with lithium chloride affords the chloro-bridged analogue, $[\{Pd[CH_2CMe_2C(=O)C_5H_4N](\mu\text{-}Cl)\}_2]$, which is converted into the corresponding mononuclear complexes by reactions with 3,5-dimethylpyridine and thallium(I) acetylacetonate. In refluxing methanol this reaction yields a new 1-methoxy-2,2-dimethyl-1-(2-pyridyl)propoxo-*N,O* type complex, $[Pd\{OC(OMe)(^tBu)C_5H_4N\}_2]$. Palladium(II) acetate reacts with 2-pivaloylpyridine in the presence of water in benzene to produce $[\{Pd[OC(OH)(^tBu)C_5H_4N](\mu\text{-}MeCO_2)\}_2]$ and $[Pd\{OC(OH)(^tBu)C_5H_4N\}_2]$.

Introduction

It is well known that unsubstituted alkyl groups are generally stable and inert towards chemical transformations. The activation of alkyl groups with transition metal compounds has become one of the leading topics in organometallic chemistry [1–3]. We have been challenging this theme through cyclometallation reactions. So far we have achieved the cyclopalladations of alkyl groups in 2-neopentylpyridine [4], *N,N*-dimethylneopentylamine [5], 2-t-butylbenzothiazole [6], and 2-(trimethylsilyl)pyridine [7] by using palladium(II) acetate as a metallating reagent.

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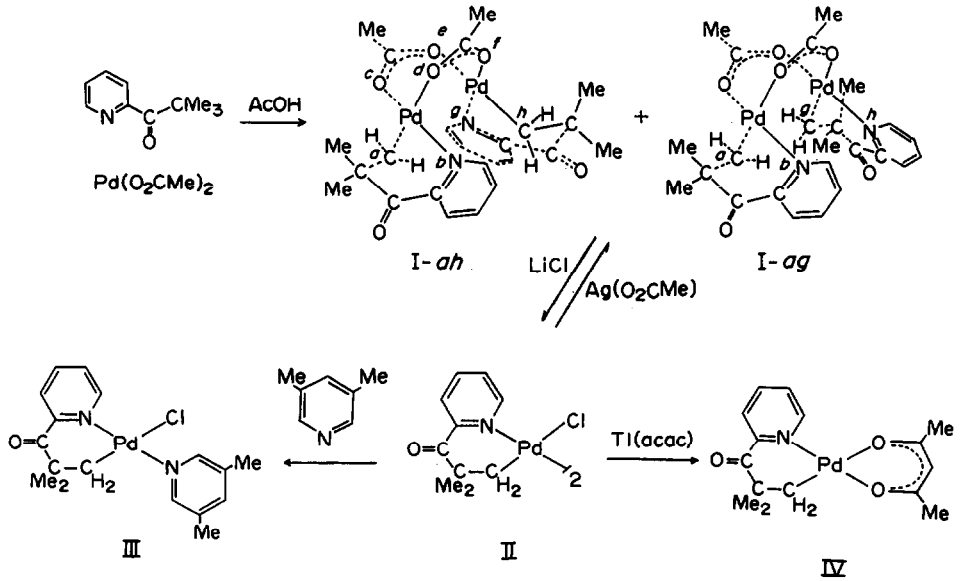
* For Part V, see ref. 7.

** Dedicated to Professor Akio Yamamoto upon retirement from the Tokyo Institute of Technology and in honor of his contributions to organometallic chemistry.



Scheme 1. Cyclometallation of 2-pivaloylpyridine. For **1**-*ah* and **1**-*ag*, dotted lines represent the groups situated behind the plane of the paper.

In this article we will report the chemical behaviour of 2-pivaloylpyridine toward palladium(II) acetate under various reaction conditions and will characterize the resulting palladium(II) complexes. Preliminary communication of these results has been made [8].

Results and discussion

Reaction in acetic acid—Formation of a novel six-membered cyclopalladated complex

2-Pivaloylpyridine reacted with palladium(II) acetate in acetic acid at 90–95 °C to afford di-μ-acetato-bis[2-methyl-2-(2-pyridylcarbonyl)propyl-C^1,N]dipalladium (II), $[\{Pd[CH_2CMe_2C(=O)C_5H_4N](\mu\text{-}MeCO_2)\}_2]$ (**1**) in 65% yield. However, **1** was contaminated with a fairly large amount of unreacted 2-pivaloylpyridine (about 16% by weight), which could not be removed even by repeated silica gel column chromatography. The contaminant was taken off when **1** was converted into the chloro-bridged analogue, $[\{Pd[CH_2CMe_2C(=O)C_5H_4N](\mu\text{-}Cl)\}_2]$ (**2**), by lithium chloride in an acetone–water solvent. By the reaction of **2** with silver(I) acetate, **1** could be reproduced in a pure state in 38% yield. Complex **2** underwent bridge-splitting reactions with 3,5-dimethylpyridine and thallium(I) acetylacetonate to yield the corresponding mononuclear cyclopalladated complexes, $[Pd\{CH_2CMe_2C(=O)C_5H_4N\}Cl(3,5\text{-}Me_2C_5H_3N)]$ (**3**) and $[Pd\{CH_2CMe_2C(=O)C_5H_4N\}(acac)]$ (**4**), respectively (Scheme 1).

All the new alkylated palladium(II) complexes, **1**–**4**, prepared in this study, show fairly high thermal stability. The IR spectra of **1**–**4** exhibited bands at about 1690 cm^{-1} due to the ν(C=O) frequency. This band is virtually the same as that of 2-pivaloylpyridine (1685 cm^{-1}), indicating that the carbonyl oxygen does not participate in coordination to palladium.

Table 1

Proton NMR data [a] for the palladium(II) complexes

Complex	Pd–CH_2	CMe_2 or CM_3 [b]	C_5H_4N moiety		Other group	
			H^6	H^3 H^5	Me	Others
1-*ah* [c]	1.00 (d) [d]	0.83, 1.10	8.86 (d) [e]	7.35 (t), [e] 7.5 (m) [f] 8.0 (m) [f]	2.03 [g]	–
1-*ag* [c]	– [h]	1.20	8.34 (d) [e]	7.02 (t), [e]	1.94 [g,i]	–
2	2.20	1.38	9.20 (d) [e]	7.55 (m), 8.02 (m)		–
3	1.87	1.33	9.79 (d) [e]	7.5 (m), 8.00 (m)	2.35	7.95, [j] 8.52, [k]
4	2.05	1.32	9.44 (d) [e]	7.5 (m), 8.03 (d) [e]	1.98, 2.01	5.35 [l]
5	–	1.17, 1.20	8.47 (d) [e]	7.24 (t), [e] 7.28 (d) [e] 7.79 (t) [e]	3.10, [m] 3.13 [m]	
6	–	0.92, 1.08 1.28	8.1 (br)	7.2–8.0 (m)	2.10, [g] 2.14 [g]	– [n]

[a] δ, relative to $SiMe_4$ in $CDCl_3$ except for **2** (CD_2Cl_2). Measured at 27 °C, except for **1**. Appearing as a singlet, unless represented in the parentheses. d = doublet, t = triplet, q = quartet, m = multiplet. [b] For **5** and **6**. [c] Measured at −20 °C. [d] ^2J(HH) = 8 Hz. Another doublet could not be detected. [e] ^3J(HH) = 6 Hz. [f] H^{3-5} protons of *ag* and *ah* isomers are overlapped with each other. [g] Acetato Me. [h] Could not be detected. [i] Another signal due to *ag* isomer overlaps with the signal at δ 2.03. [j] γ-H of the pyridine ring. [k] α-H of the pyridine ring. [l] Acac-CH. [m] Methoxy-Me. [n] Signals due to OH proton could not be detected.

The IR spectrum of **1** showed two bands at 1570 and 1410 cm^{-1} characteristic of bridging acetato ligand [9]. As for the ^1H NMR spectrum of **1** at −20 °C, two sets of signals were observed (Table 1). One set consisted of signals at δ 0.83 (s, 4.8H, CCH_3), 1.10 (s, 4.8H, CCH_3), 2.03, (s, 4.8H, CH_3CO_2) and 8.86 (d, 1.6H, 6-H of the pyridine ring). Upon heating at 28 °C, the two singlets at 0.83 and 1.10 coalesced to a singlet at δ 0.98 [9.6H, $C(CH_3)_2$]. However, the other set exhibited signals at δ 1.20 [s, 2.4H, $C(CH_3)_2$], 1.94 (s, 0.6H, CH_3CO_2), * and 8.34 (d, 0.4H, 6-H of the pyridine ring) at −20 °C, showing no temperature-dependency in the range of −20–28 °C. These data indicate that **1** consists of two isomers in a molar ratio of about 4:1. In consideration of the acetato methyl signals [4], the former set was assigned to an *a,h*-C^1; *b,g*-N (*ah*) type isomer with a C_2 symmetry, whereas the latter was of *a,g*-C^1; *b,h*-N (*ag*) type with C_s symmetry, as shown in Scheme 1.

The monocuclear cyclopalladated complexes, **3** and **4**, did not show any temperature-dependent ^1H NMR spectra in the range of −50–28 °C, indicating that the flopping motion of the six-membered chelate ring Pd–CH_2–CMe_2–C(=O)–C⋯N is rapid even at −50 °C. Accordingly, the temperature-dependent ^1H NMR spectra of **1**-*ah* are ascribed to acetato-bridge inversion. Similar inversion of acetato-bridges has already been reported about $[\{Pd(\mu\text{-}MeCO_2)(\eta^3\text{-}C_3H_5)\}_2]$ [10], $[\{Pd(\mu\text{-}MeCO_2)Cl(PMe_2Ph)\}_2]$ [11], and $[\{Pd(CH_2C_9H_6N)(\mu\text{-}MeCO_2)\}_2]$ (C_9H_6N = 8-quinolyl) [12].

In the slow exchange limit at −20 °C, each of two Pd–CH_2–CMe_2 moieties of **1**-*ah* experiences anisotropic shielding from the pyridine ring which is situated over

* Another signal of the acetate-methyl protons probably overlaps with the signal at δ 2.03 for the former set.

the Pd–CH_2–CMe_2 moiety in the folded structure of the acetato-bridged dimer [13]. By this shielding effect, the two kinds of methyl protons in **1**-*ah* resonated as the two singlets at δ 0.83 and 1.10 (see above). At high temperature where acetato-bridge inversion is rapid, the two kinds of methyl protons appear as a singlet at δ 0.98. On the other hand, two Pd–CH_2–CMe_2 moieties in **1**-*ag* are located face to face and are not subject to enough anisotropy to differentiate the two methyl groups.

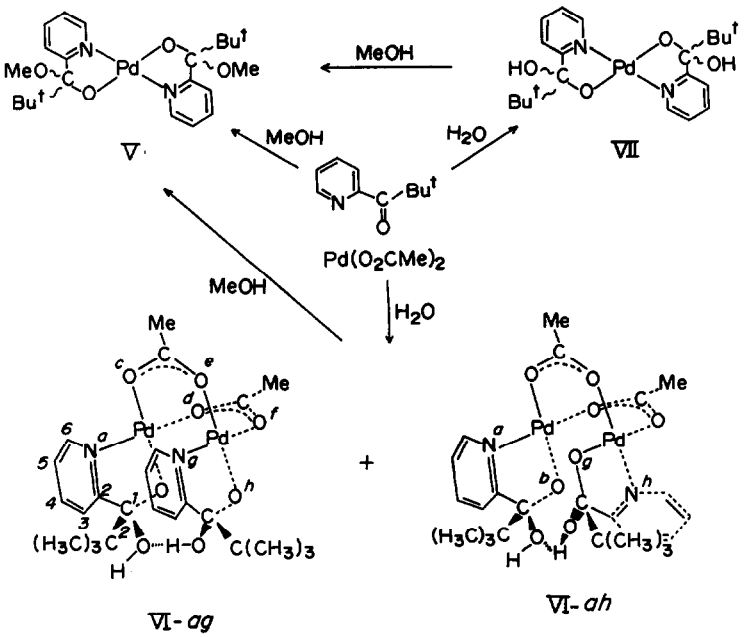
As for the ^{1}H NMR spectrum of **2**–**4**, methylene protons were detected clearly in the range of δ 1.80–2.20, supporting the cyclopalladated structure. In particular, the methylene protons of **3** appeared at slightly high field (δ 1.87) compared with those of **2** (δ 2.10) and **4** (δ 2.05). This is associated with the shielding effect of the adjacent 3,5-dimethylpyridine ring. The IR spectrum of **4** showed two characteristic bands of *O,O'*-chelating acac ligand at 1590 and 1450 cm^{-1}. Its mass spectrum gave a parent ion peak at *m/e* 367 corresponding to [^{106}Pd{CH_2CMe_2C(=O)-C_5H_4N}(acac)] and a fragment ion peak at *m/e* 268 due to [^{106}Pd{CH_2CMe_2C-(=O)C_5H_4N}]$^+$.

*Reaction with methanol or water—formation of [1-methoxy- or 1-hydroxy-2,2-dimethyl-1-(2-pyridyl)propoxo-*N,O*]palladium(II) complexes*

2-Pivaloylpyridine reacted in refluxing methanol with palladium(II) acetate to afford yellow crystals **5**. Its IR spectrum lacked the ν(C=O) and the ν(COO) frequencies due to the carbonyl and the acetato groups, respectively, and instead strong ν(C–O) frequencies appeared newly at 1100, 1040, and 1015 cm^{-1}. As for the ^{1}H NMR spectrum (Table 1), methoxy protons were observed as two singlets at δ 3.10 (4.5H) and 3.13 (1.5H), together with t-butyl protons at δ 1.17 (s, 4.5H) and 1.20 (s, 13.5H). On the basis of these results and of elemental analysis, **5** was assigned to bis[1-methoxy-2,2-dimethyl-1-(2-pyridyl)propoxo-*N,O*]palladium(II), [Pd{OC(OMe)(^{t}Bu)C_5H_4N}$_2$] (Scheme 2). The two sets of signals for the ^{t}Bu group and the OMe signal in the ^{1}H NMR spectrum indicate that **5** consists of two isomers in the population ratio of about 3 : 1. *Trans*- and *cis*-forms are possible for the isomers of bis(*N,O*-chelate)palladium(II) complexes such as **5**. As bis(*N,O*-chelate)palladium(II) complexes like bis(salicyl-aldiminato)- and bis(semicarbazonato)palladium(II) have been reported to *trans* forms [14], **5** was ascribed to the *trans* form. The two isomers of **5** were assigned to C_i and C_2 symmetry forms caused by two asymmetric carbons (Scheme 2). The ^{13}C{^{1}H} NMR spectrum of **5** was assigned (Table 2) referring to those of 2-ethylpyridine [15] and acetaldehyde diethylacetal (CH, δ 99.5) [15].

In the temperature range of 30–35 °C in benzene, 2-pivaloylpyridine reacted with palladium(II) acetate in the presence of water in amounts equimolar with palladium(II) acetate to give an acetato-bridged binuclear [1-hydroxy-2,2-dimethyl-1-(2-pyridyl)propoxo-*N,O*]palladium(II) complex, [{Pd[OC(OH)(^{t}Bu)C_5H_4N](μ-$MeCO_2$)}$_2$] (**6**) (Scheme 2). On the other hand, the reaction between 2-pivaloylpyridine and palladium(II) acetate produced precipitates of [Pd{OC(OH)(^{t}Bu)-C_5H_4N}$_2$] (**7**) in the presence of excess water in THF. The analogous reaction in a benzene–water suspension afforded **6** besides **7** even in the presence of excess water.

The IR spectrum of **6** showed two characteristic bridging acetato bands at 1555 (s) and 1430 (s) cm^{-1}, together with the ν(C–O) frequencies at 1130 (s), 1095 (s),



Scheme 2. Syntheses and reactions of [2,2-dimethyl-1-(2-pyridyl)propoxo-*N*,*O*]palladium(II) complexes. For **6**-*ag* and **6**-*ah*, dotted lines represent the groups situated behind the plane of the paper. Carbon numbers for propyl and pyridyl groups are in italics.

and 1000 (s) cm^{-1}. Furthermore, **6** exhibited broad bands at 3440 and 3240 cm^{-1}, ascribable to ν(OH) frequencies without and with hydrogen bonding, respectively. Acetato-bridged binuclear palladium(II) complexes have a folded structure of two palladium-coordination planes with a dihedral angle of about 24° [13]. The two *t*-butyl groups in **6** are too bulky to be situated inside the palladium-coordination planes in the folded structure.

They are, therefore, certainly located at the outer sides of the palladium-coordination planes. As for the ^1H NMR spectrum of **6**, *t*-butyl protons appeared as three singlets at 0.92 (6H), 1.08 (3H), and 1.28 (9H). The $^{13}C\{^1H\}$ NMR spectrum of **6** showed that each of 1- and 2-carbons of propoxo group and 2- and 6-carbons of pyridyl group appeared as four singlets (Table 2). These facts indicate that **6** consists of *a*,*g*-N; *b*,*h*-O (*ag*) and *a*,*h*-N; *b*,*g*-O (*ah*) type isomers, each of which has two magnetically nonequivalent 1-hydroxy-2,2-dimethyl-1-(2-pyridyl)propoxo-*N*,*O* chelates (Scheme 2). Molecular models indicate that the *ag*-type forms a more preferable hydrogen bond compared with the *ah*-type, in consideration of the lengths of O–H · · · O. The singlets at δ 0.92 and 1.28 (two third parts of 9H) are ascribed to **6**-*ag*, whereas the singlets at δ 1.08 and 1.28 (the remaining part of 9H) are due to **6**-*ah*. The population ratio of **6**-*ag* and -*ah* is about 2:1. Complex **6** did not show temperature-dependent ^1H NMR spectra in the range 28–60 °C, revealing the absence of the acetato-bridge inversion in **6**. Moreover, **6** was converted to **5** by heating in methanol for 2.5 h.

Complex **7** was almost insoluble in common organic solvents. The IR spectrum of **7** showed four strong ν(C–O) frequencies at 1125, 1090, 1045, and 1015 cm^{-1} and a broad ν(OH) band at 3130 cm^{-1}, assignable to hydrogen bonding. The

Table 2

$^{13}C\{^1H\}$ data [a] for **5** and **6**

Compound	Pd–$OC^1(OR)$–$C^2(CH_3)_3$				C_5H_4N moiety					Acetato	
	1-C	2-C	$(CH_3)_3$	OCH_3	2-C	3-C	4-C	5-C	6-C	CH_3	CO_2
5	113.0	41.0 [b]	26.3	49.1	170.5	125.3	136.9	123.3	147.9	–	–
	113.2 [b]	41.2		50.1 [b]			137.0 [b]		148.1 [b]		
6	110.9	39.9 [b]	25.5	–	167.5	125.8	138.3	123.5	145.0 [b]	23.0	172.8
	111.4	40.2	25.9		167.8	126.1	139.5	124.0	145.3	23.3	182.9
	111.8 [b]	40.3			168.7 [b]	128.3		124.2	147.3 [b]	23.6	183.7
	112.3 [b]	40.4 [b]			170.9 [b]				147.5		
2-Ethyl-pyridine [c]	–	–	–	–	163.4	121.8	136.1	120.7	149.7	–	–

[a] δ, Relative to $SiMe_4$ in $CDCl_3$. [b] Ascribed to the minor component. As for the other signals, the minor ones could not be distinguished. [c] Ref. [15].

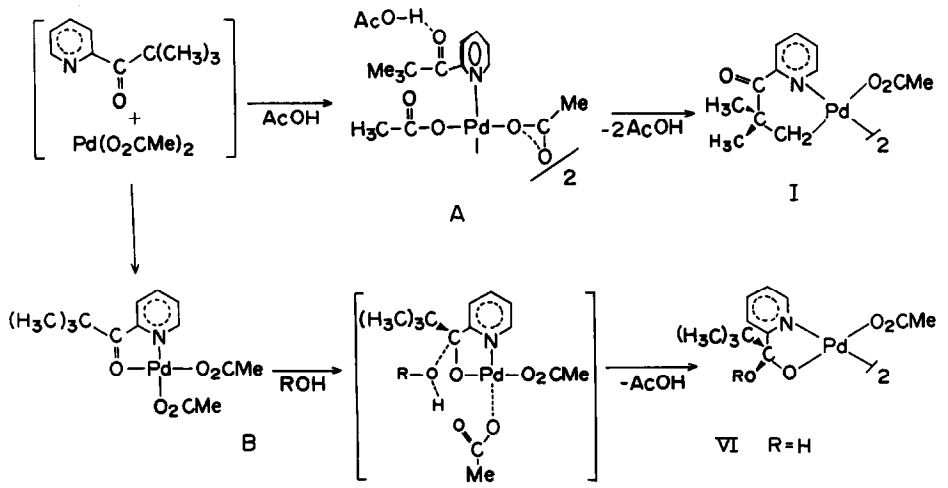


Fig. 1. Possible mechanisms for cyclopalladation and for the nucleophilic attack on the carbonyl carbon.

insolubility of **7** is probably due to intermolecular association by the hydrogen bonding. Complex **7** also reacted with refluxing methanol to give **5** in 85% yield.

Proposed mechanisms

It is noteworthy that 2-pivaloylpyridine reacted with palladium(II) acetate to afford four types of complexes: the six-membered cyclopalladated complex **1** and [1-methoxy- and 1-hydroxy-2,2-dimethyl-1-(2-pyridyl)propoxo-*N*,*O*]palladium(II) complexes **5**–**7**. These different reaction modes of 2-pivaloylpyridine toward palladium(II) acetate can be explained as follows.

In acetic acid, the pyridyl nitrogen of 2-pivaloylpyridine is coordinated to the palladium atom. The coordination ability of carbonyl oxygen is suppressed owing to hydrogen bonding with an acidic proton (intermediate A in Fig. 1). The palladium atom attacks a neighbouring methyl group of the bulky *t*-butyl moiety probably in an electrophilic fashion, resulting in the formation of the palladium-methylene bond. Thus, the methyl group, which is stable in general and not liable to chemical transformation, is metallated in mild conditions to form the six-membered chelate, Pd–$CH_2CMe_2C(=O)C_5H_4N$. It has been reported that the palladium atom acts presumably as an electrophilic centre in the cyclopalladation of 8-alkylquinolines [12]. Indeed, we found that palladium atom of palladium(II) acetate attacked an electron-rich carbon (C-2) of 4-methyl-4′-nitrodibenzyl sulphide to give rise to cylopalladation [16].

On the other hand, in methanol or a benzene–water mixed solvent, 2-pivaloylpyridine is coordinated to palladium atom with both pyridyl nitrogen and carbonyl oxygen sites (intermediate B). The carbonyl carbon in coordinated 2-pivaloylpyridine is susceptible to nucleophilic attack and reacts with ROH species (R = methyl or H) or hydroxy anion. The [1-methoxy- or 1-hydroxy-2,2-dimethyl-1-(2-pyridyl)propoxo-*N*,*O*]palladium(II) complex such as **5**, **6**, or **7** is formed through this mechanism.

Fukuda et al. investigated a reaction between $[Co(hfac)(en)_2]^{2+}$ (hfac = 1,1,1,5,5,5-hexafluoropentan-2,4-dionato-*O*,*O*′) and hydroxide ion and detected a

Table 3

Yields and elemental analyses of the palladium complexes

Complex	Yield (%)	M.p. [a] (°C)	Analysis [b] (%)		
			C	H	N
1	38 [c]	141	44.1 (44.0)	4.65 (4.6)	4.30 (4.3)
2	83	120	39.0 (39.5)	3.95 (4.0)	4.25 (4.6)
3	60	141	49.65 (49.65)	5.25 (5.15)	6.75 (6.8)
4	42	114	48.4 (49.0)	5.2 (5.2)	3.8 (3.8)
5	31 [d,e]	145	53.0 (53.4)	6.65 (6.5)	5.45 (5.65)
6	39 [d]	150	42.25 (41.7)	4.95 (4.95)	4.3 (4.05)
7	41 [d]	190	50.5 (51.45)	6.1 (6.05)	5.85 (6.0)

[a] With decomposition. [b] Calculated values are given in parentheses. [c] Based on **2**. See text. [d] Based on $Pd(O_2CMe)_2$. [e] 56% yield based on 2-pivaloylpyridine.

1,1,1,5,5,5-hexafluoro-4-hydroxy-2-penten-2,4-diolato-*O,O'* chelation [17], which contained a structure with similarities to the 1-(2-pyridyl)-1-hydroxyalkoxo-*N,O* chelation elucidated in the previous communication [8] and the present study. The chelation of $[Co(hfac\ OH)(en)_2]Br \cdot H_2O$ which was inferred [17] was later confirmed by X-ray structural analysis [18]. Addition of a protic molecule such as alcohol or water had been found in the cases of di-2-pyridyl ketone coordinated to palladium(II) and gold(III) [19] and of a macrocyclic di-imine coordinated to nickel [20].

Experimental

All the experiments were carried out under dry nitrogen. Solvents were dried by usual methods and distilled. 2-Pivaloylpyridine and thallium(I) acetylacetonate were prepared according to the literature [21,22]. The other reagents were obtained commercially and used without further purification.

IR spectra were measured on a Hitachi model 285 spectrophotometer. ^1H- and ^{13}C-NMR spectra were recorded on JEOL JNM-MH-100 and FX-90Q spectrometers, respectively, using tetramethylsilane as an internal standard. Molecular weight was determined in benzene with a Corona model 114 molecular weight apparatus at 41.8 °C. Melting points were determined with a Yanaco micro melting point apparatus and are uncorrected. Mass spectra were obtained with a Nichiden-Varian TE-600 gaschromatograph-mass spectrometer. The yields and microanalytical data of the new complexes obtained in this study are summarized in Table 3.

Preparation of cylopalladated complexes

$[\{Pd[CH_2CMe_2C(=O)C_5H_4N](\mu\text{-}MeCO_2)\}_2]$, 1. (i) An acetic acid suspension (30 cm^3) containing palladium(II) acetate (4.45 mmol) and 2-pivaloylpyridine (4.9 mmol) was heated at 90–95 °C for 5 h. The resulting mixture was evaporated to dryness to give a brown oil, which was chromatographed on a silica gel column (200 mesh, $12\phi \times 220$ mm). A yellow fraction eluted by diethyl ether/methanol (3:1) was evaporated to dryness. The residue (1.13 g) consisted of **1** (0.95 g, 65%) and 2-pivaloylpyridine (0.28 g), estimated by its ^1H NMR spectrum. The 2-pivaloylpyridine component could not be removed by repeated column chromatographic purification.

(ii) Silver acetate (0.87 mmol) was added to an acetone solution of **2** (0.40 mmol), and then the mixture was stirred at room temperature for 1 d. After centrifugation of the reaction mixture, the resulting supernatant was diluted with hexane to give **1** as a yellow solid.

Preparation of $[\{Pd[CH_2CMe_2C(=O)C_5H_4N]Cl\}_2]$ **2.** An acetone–water (15 cm^3/1 cm^3) suspension containing **1** (0.71 mmol) and LiCl (7.7 mmol) was stirred for 15 h. The precipitated pale yellow solid was collected, and washed with a methanol/water (10 cm^3/10 cm^3) mixture to afford **2**.

Preparation of $[Pd\{CH_2CMe_2C(=O)C_5H_4N\}Cl(3,5\text{-}Me_2C_5H_3N)]$ **3.** A solution in dichloromethane (15 cm^3) of **2** (0.16 mmol) and 3,5-dimethylpyridine (0.40 mmol) was stirred for 17 h. Addition of hexane to the resulting mixture yielded **3** as pale yellow crystals.

Preparation of $[Pd\{CH_2CMe_2C(=O)C_5H_4N\}(acac)]$ **4.** A dichloromethane suspension (15 cm^3) containing **2** (0.33 mmol) and Tl(acac) (0.73 mmol) was stirred at room temperature for 16 h. After centrifuging the resulting suspension, the supernatant was passed through a silica gel column (200 mesh, 13ϕ × 50 mm) with dichloromethane as an eluent. A pale-yellow fraction was collected, concentrated under reduced pressure, and diluted with hexane to produce **4** as yellow crystals.

*Preparation of [2,2-dimethyl-1-(2-pyridyl)propoxo-*N,O*]-palladium(II) complexes*

$[Pd\{OC(OMe)(^tBu)C_5H_4N\}_2]$, **5.** A methanol suspension (15 cm^3) containing palladium(II) acetate (1.1 mmol) and 2-pivaloylpyridine (1.2 mmol) was refluxed for 1 h. After filtering precipitated palladium black from the suspension, the filtrate was concentrated under reduced pressure to afford **5** as yellow needles.

Preparation of $[\{Pd[OC(OH)(^tBu)C_5H_4N](\mu\text{-}MeCO_2)\}_2]$, **6.** A wet benzene suspension (15 cm^3; containing 1.2 mmol of H_2O) of palladium(II) acetate (1.1 mmol) and 2-pivaloylpyridine (2.2 mmol) was stirred at 30–35 °C for 24 h. After filtration, the filtrate was concentrated and diluted with hexane to afford a yellow solid, **6**.

Preparation of $[Pd\{OC(OH)(^tBu)C_5H_4N\}_2]$, **7.** A THF–water (15 cm^3/2 cm^3) suspension containing palladium(II) acetate (1.1 mmol) and 2-pivaloylpyridine (2.2 mmol) was stirred at 30–35 °C for 17 h. An off-white solid was precipitated and collected and washed with dichloromethane to give **7**.

Reaction of palladium(II) acetate with 2-pivaloylpyridine in benzene–water mixed solvent

A benzene–water (15 cm^3/5 cm^3) suspension containing palladium(II) acetate (1.1 mmol) and 2-pivaloylpyridine (2.2 mmol) was stirred at 30–35 °C for 23 h. The resulting mixture was filtered to give an off-white cake and a yellow-orange bilayer filtrate. The cake was washed with methanol to give **7** in 43% yield (based on $Pd(O_2CMe)_2$). The benzene solution was separated from the bilayer filtrate and diluted with hexane to yield **6** in 21% yield [based on $Pd(MeCO_2)_2$].

Reaction of **6** *with methanol*

A methanol solution (15 cm^3) of **6** (0.19 mmol) was refluxed for 2.5 h. After filtering precipitated palladium black from the resulting mixture, the filtrate was concentrated under reduced pressure to give **5** in 30% yield based on **6**. This yield

corresponds to 60% based on 1-hydroxy-2,2-dimethyl-1-(2-pyridyl)propoxo-*N,O* moiety.

Reaction of 7 with methanol

A methanol suspension (10 cm^3) of **7** (0.21 mmol) was refluxed for 1.5 h. After filtration, the filtrate was concentrated to give **5** in 85% yield based on **7**.

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References

1 J. Halpern, Discuss. Faraday Soc., 46 (1968) 7.
2 D.E. Webster, Adv. Organomet. Chem., 15 (1977) 147.
3 A.E. Shilov, Activation of Saturated Hydrocarbons by Transition Metal Complexes, D. Reidel, Dordrecht, 1984.
4 Y. Fuchita, K. Hiraki and T. Uchiyama, J. Chem. Soc., Dalton Trans., (1983) 897.
5 Y. Fuchita, K. Hiraki and Y. Matsumoto, J. Organomet. Chem., 280 (1985) C51.
6 K. Hiraki, Y. Fuchita, M. Nakashima and H. Hiraki, Bull. Chem. Soc. Jpn., 59 (1986) 3073.
7 Y. Fuchita, M. Nakashima, K. Hiraki, M. Kawatani and K. Ohnuma, J. Chem. Soc., Dalton Trans., (1988) 785.
8 K. Hiraki, Y. Fuchita and M. Nakashima, Inorg. Chim. Acta, 97 (1985) L15.
9 H. Onoue and I. Moritani, J. Organomet. Chem., 43 (1972) 431.
10 J. Powell, J. Am. Chem. Soc., 91 (1969) 4311.
11 J. Powell and T. Jack, Inorg. Chem., 11 (1972) 1039.
12 A.J. Deeming and I.P. Rothwell, J. Organomet. Chem., 205 (1981) 117.
13 M.R. Churchill, H.J. Wasserman and G.J. Young, Inorg. Chem., 19 (1980) 762.
14 C.F.J. Barnard and M.J.H. Russell, in G. Wilkinson, R.D. Gillard and J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, Vol. 5, Pergamon Press, Oxford, 1987, p. 1099.
15 L.F. Johnson and W.C. Jankowski, Carbon-13 NMR Spectra, Wiley, New York, 1972.
16 K. Hiraki, Y. Fuchita and Y. Kage, J. Chem. Soc., Dalton Trans., (1984) 99.
17 Y. Fukuda, M. Ishige, T. Ito, K. Kuroda, K. Sone, Y. Suzuki, S. Yano and S. Yoshikawa, Chem. Lett., (1981) 1699.
18 S. Aygen, E.F. Paulus, Y. Kitamura and R. van Eldik, Inorg. Chem., 26 (1987) 769.
19 G. Annibale, L. Canovese, L. Cattalini, G. Natile, M. Biagini-Cingi, A. Manotti-Lanfredi and A. Tiripicchio, J. Chem. Soc., Dalton Trans., (1981) 2280.
20 C. Cairns, S.G. McFall, S.M. Nelson and M.G.B. Drew, J. Chem. Soc., Dalton Trans., (1979) 446.
21 R. Bokalski and A.R. Katritzky, J. Chem. Soc. B, (1968) 836.
22 W.H. Nelson, W.J. Randall and D.F. Martin, Inorg. Synth., 9 (1971) 53.