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Reactions of 2-Pivaloylpyridine with Palladium(II) Acetate Resulting in the Formation of [1-Methoxy- and 1-Hydroxy-2,2-dimethyl-1-(2-pyridyl)propoxo-*N*,*O*]palladium(II) Complexes

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We investigated the cyclopalladation of alkyl-substituted Lewis bases by palladium(II) acetate [1, 2], because of interest in the activation of C–H bond by transition metal compounds [3]. Recently, 2-pivaloylpyridine has been found to react with palladium(II) acetate in acetic acid to give a six-membered cyclopalladated complex, $[\{\overline{\mathrm{Pd}(\mathrm{CH_2CMe_2COC_5H_4N}})(\mu\text{-}\mathrm{CO_2Me})\}_2]$ [4]. In this paper, we report novel *N*,*O*-chelating complexes, [1-methoxy- and 1-hydroxy-2,2-dimethyl-1-(2-pyridyl)propoxo-*N*,*O*]palladium(II) ones, produced from the reactions of palladium(II) acetate with 2-pivaloylpyridine in methanol and an aqueous tetrahydrofuran solution.

A methanol suspension (15 ml) containing palladium(II) acetate (1.1 mmol) and 2-pivaloylpyridine (1.2 mmol) was refluxed for 1 h. After filtering the suspension to remove precipitated palladium black, the filtrate was concentrated under reduced pressure to afford yellow needles, $[\mathrm{Pd}\{\mathrm{OCBu^t(OMe)C_5H_4N}\}_2]$ (I)**, in 31% yield based on $\mathrm{Pd(CH_3CO_2)_2}$. The IR spectrum of I lacked the ν(COO) frequencies due to acetate ligands, and instead strong ν(C–O) frequencies appeared at 1120, 1040 and 1015 $\mathrm{cm^{-1}}$. As for the ^{1}H NMR spectrum of I in $\mathrm{CDCl_3}$, t-butyl protons appeared as two singlets at δ(ppm) 1.17 (s, 4.5H) and 1.20 (s, 13.5H) together wtih the pyridyl protons at δ 7.25 (m, 4H, H^3 and H^4 or H^5), 7.79 (t, 2H, H^4 or H^5), and 8.47 (d, 2H, H^6). In addition, methoxy protons were newly observed at δ 3.10 (4.5H) and 3.13 (1.5H). On the basis of these results and elemental analysis, **I** was assigned to bis[1-methoxy-2,2-dimethyl-1-(2-pyridyl)propoxo-*N*,*O*]palladium(II). Two sets of signals for $\mathrm{Bu^t}$ and OMe groups in the ^{1}H NMR spectrum indicate that **I** consists of two diastereomers, racemic and meso forms in the population ratio of about 3:1.

The $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectrum of **I** was assigned referring to those of 2-ethylpyridine [5] (Table I) and acetaldehyde diethylacetal $[\mathrm{CH_3Ch(OEt)_2}$, δ 99.5] [5]. In the ^{13}C NMR spectrum of **I**, two sets of signals were also observed for 1-C, 2-C, $\mathrm{OCH_3}$, 4-C, and 6-C, confirming the presence of two diastereomers in **I**.

When the reaction between 2-pivaloylpyridine (2.2 mmol) and palladium(II) acetate (1.1 mmol) was carried out in aqueous THF ($\mathrm{THF/H_2O}$ = 15 ml/2 ml), an off-white solid precipitated after stirring for 17 h at 30–35 °C. This solid was filtered and washed with dichloromethane to give $[\mathrm{Pd}\{\mathrm{OCBu^t(OH)C_5H_4N}\}_2]_n$ (**II**)§ in 41% yield based on $\mathrm{Pd(CH_3CO_2)_2}$. Complex **II** is almost insoluble in common organic solvents. The IR spectrum of **II** showed four strong ν(C–O) frequencies at 1125, 1090, 1045 and 1015 $\mathrm{cm^{-1}}$ and a broad ν(OH) band at 3120 $\mathrm{cm^{-1}}$, assignable to a hydrogen bond. The insolubility of **II** is probably due to intermolecular association by the hydrogen bond.

It is noteworthy that 2-pivaloylpyridine shows different reaction modes towards palladium(II) acetate depending on the solvents used. A cyclometallation occurred in acetic acid [4], and a nucleophilic attack of methoxide or hydroxide ion to coordinated 2-pivaloylpyridine did in methanol and aqueous THF to produce **I** and **II**, respectively. Though addition of protic molecules such as alcohol or water has been found in the cases of di-2-pyridyl ketone coordinated to palladium(II) and gold(III) [6] and of a macrocyclic di-imine coordinated to nickel(II) [7], it is the first time to our knowledge that 1-methoxy- and 1-hydroxy-alkoxo transition metal complexes, such as **I** and **II**, have been obtained.

TABLE I. $^{13}\mathrm{C}\{^1\mathrm{H}\}$NMR Data[a] for (I) and 2-Ethylpyridine.[b]

Compound	$\mathrm{Pd{-}O{-}C^1(OCH_3)C^2(CH_3)_3}$				$\mathrm{C_5H_4N}$ moiety				
	1-C	2-C	$\mathrm{(CH_3)_3}$	$\mathrm{OCH_3}$	2-C	3-C	4-C	5-C	6-C
(I)	113.0 113.2	41.0 41.2	26.3	49.1 50.1	170.5	125.3	136.9 137.0	123.3	147.9 148.1
2-Ethylpyridine	–	–	–	–	163.4	121.8	136.1	120.7	149.7

[a] Recorded on a JEOL FX-90Q spectrometer. δ-Value relative to TMS in $\mathrm{CDCl_3}$. [b] Ref. 5.

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**The melting point of I was 150 °C.

§The melting point of II was 190 °C.

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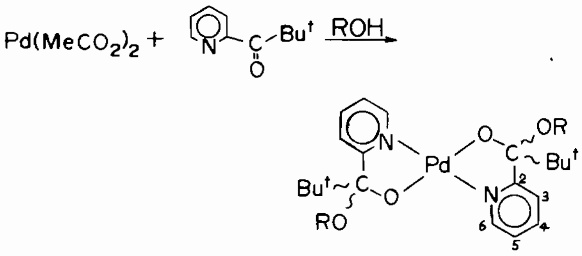

I R = Me
II R = H

Scheme 1. Reactions of 2-pivaloylpyridine with palladium(II) acetate.

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