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[1-(2-Pyridyl)alkoxo-N,O] ruthenium(II) Complexes Derived from a Carbonylchlorohydridoruthenium(II) Complex and 2-Acylpyridines

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2-Formylpyridine was inserted into the hydrido–ruthenium bond in [RuClH(CO)(PPh$_3$)$_3$] at room temperature to give cis-*[RuCl(OCH$_2$-C$_5$H$_4$N-N,O)-(CO)(PPh$_3$)$_2$] (II). Complex II isomerized in refluxing benzene to a thermodynamically-stable* trans *form. 2-Acetyl- and 2-benzoylpyridines also reacted with [RuClH(CO)(PPh$_3$)$_3$] in refluxing THF to afford insertion products, [RuCl(OCHR-C$_5$H$_4$N-N,O](CO)(PPh$_3$)$_2$] (R = Me and Ph, respectively). These complexes were characterized by means of elemental analysis, molecular weights, and IR and NMR spectroscopy.*

Introduction

It has been reported that carbonylchlorohydridotris(triphenylphosphine)ruthenium(II) (I) reacts with arenediazonium compounds [1], carbon disulfide [2], organic isothiocyanate [3], diarylcarbodiimides [4], and substituted olefins [5] to yield the corresponding insertion products, and with diisopropylcarbodiimide to give an insertion product followed by dehydrogenation [6]. Recently, Yamamoto *et al.* [7] found that [RuH$_2$(PPh$_3$)$_4$] and I catalyzed Tischenko-type reactions of aldehydes, and obtained two diacylruthenium(II) complexes from the reaction of [RuH$_2$(PPh$_3$)$_4$] with propionaldehyde. It is interesting to investigate the reactions of I towards 2-acylpyridines, as compared with the Tischenko-type reactions catalyzed by I [7].

The present paper deals with reactions of I with 2-acylpyridines and with the resulting [1-(2-pyridyl)-alkoxo-N,O] ruthenium(II) complexes.

Experimental

Complex I was prepared according to a literature method [8]. The molecular weight of a complex was determined in benzene using a Corona model 114 vapour pressure osmometer. ^{13}C- and ^{31}P-NMR spectra were run on JEOL model JNM-FT 90Q and 60Q spectrometers, respectively. The other procedures were as described in an earlier paper [9].

Reaction of I with 2-Formylpyridine

A THF suspension (30 ml) containing I (0.50 mmol) and 2-formylpyridine (2.0 mmol) was stirred at room temperature for 26 h to yield an olive–yellow solution. After concentration, the solution was diluted with hexane to cause precipitation. The precipitate was collected and washed with hexane to give a pale yellow–green solid, *cis*-[RuCl(OCH$_2$-C$_5$H$_4$N)(CO)(PPh$_3$)$_2$] (**II**).

Isomerization of II

A benzene suspension (30 ml) of II (0.22 mmol) was refluxed for 3 h to give a brownish-purple solution. After concentration, the solution was diluted with hexane. The resulting olive solid was recrystallized from benzene and hexane to afford a dull-yellow orange crystal, *trans*-[RuCl(OCH$_2$-C$_5$H$_4$N)-(CO)(PPh$_3$)$_2$] (**III**) in 81% yield. Complex III was also obtained directly by the reaction of I with 2-formylpyridine in refluxing benzene for 2 h.

Reaction of I with 2-Acetylpyridine

A THF suspension (30 ml) containing I (0.50 mmol) and 2-acetylpyridine (2.0 mmol) was refluxed for 3 h, resulting in a dark green solution. After filtration, the solution was concentrated and diluted with hexane to give a yellowish-green powder, [RuCl-(OCHMe-C$_5$H$_4$N)(CO)(PPh$_3$)$_2$] (**IV**).

Reaction of I with 2-Benzoylpyridine

A THF suspension (30 ml) containing I (0.50 mmol) and 2-benzoylpyridine (1.50 mmol) was stirred at 55 °C for 4 h to yield a deep green solution. After filtration, the filtrate was evacuated to dryness *in vacuo*. The residue was chromatographed on a column (14 cm length) of Wako-gel C-200 with benzene as an eluent to give a yellow solid, [RuCl-OCHPh-C$_5$H$_4$N)(CO)(PPh$_3$)$_2$] (**V**). Molecular weight, Found: 860; Calcd for C$_{49}$H$_{40}$NO$_2$P$_2$ClRu: 873.3.

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TABLE I. Yields, Elemental Analyses and the Selected ^{1}H-NMR Data.

Complex	Yield[a] (%)	Mp. (°C)	Elemental Analyses (%)[b]			^{1}H-NMR (δ/ppm)[c]	
			C	H	N	Alkoxo group	Pyridyl group[d]
II	93	135	64.85 (64.78)	4.72 (4.55)	1.91 (1.76)	4.91 d[e], 5.63 d[e]	6.72 d, 8.56 d[f]
III	46	185–195	64.64 (64.78)	4.52 (4.55)	2.01 (1.76)	4.81 s	6.15 t, 6.25 d, 7.00 t, 8.50 d
IV	42	220	64.52 (65.22)	4.66 (4.60)	1.70 (1.73)	4.01 q[g], 0.85 d[g]	6.18 d, 6.59 t[f], 8.60 d
V	23	184–186	67.41 (67.39)	4.69 (4.62)	1.69 (1.60)	4.90 s	5.95 d, 6.40 t, 6.95 t, 8.30 d

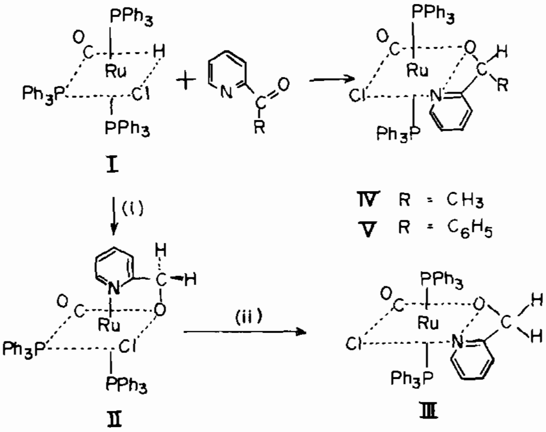
[a] Based on I. [b] Calculated values in parentheses. [c] In CD_2Cl_2 for II–IV, and in $CDCl_3$ for V. Phenyl proton resonances are omitted. [d] $^3J(HH)$ = *ca.* 8 Hz for each proton. [e] An AB type with $^2J(HH)$ = 17 Hz. [f] The other triplet was obscured by the phenyl proton resonances. [g] $^3J(HH)$ = 6 Hz.

Results and Discussion

The hydridoruthenium(II) complex I reacted smoothly with 2-formylpyridine in THF at room temperature to give *cis*-[RuCl(OCH$_2$-C$_5$H$_4$N)(CO)(PPh$_3$)$_2$] **II** in a high yield. Complex II isomerized to *trans*-[RuCl(OCH$_2$-C$_5$H$_4$N)(CO)(PPh$_3$)$_2$] **III** in refluxing benzene *(vide infra)*. However, the compound I did not react with 2-acetyl- or 2-benzolylpyridine at room temperature, but reacted at higher temperature to afford the corresponding alkoxo complexes IV and V, respectively. Yields, elemental analyses, and selected ^{1}H-NMR data of II–V are summarized in Table I.

The IR spectra of II–V lacked both the ν(H–Ru) band, which had been observed in the starting complex, I [8], and a ν(C=O) band expected for the 2-acylpyridines. On the other hand, they showed four strong bands near 1930, 1480, 1440, and 1095 cm^{-1} attributable to ν(C≡O), phenyl group, ν[P–C-(aromatic)], and ν(C–O), respectively, and as well as a weak band near 1620 cm^{-1}, assignable to the ν(C=N), of the pyridine ring. The ^{1}H-NMR spectra of II–V exhibited the resonance of a methylene (for II and III) or methine (for IV and V) group, adjacent to oxygen atom (Table I). These data indicate unambiguously that 2-acylpyridines are inserted into the hydrido–ruthenium bond of I to yield an alkoxo–ruthenium bond.

Complexes II–V are stable in the solid state in air, whereas II begins to decompose in dichloromethane under nitrogen atmosphere after several hours. Such stability of the alkoxo–ruthenium bond in II–V is possibly attributable both to the chelate effect, assisted by the coordination of the pyridyl group, and to the electron delocalization effect due to the coordination of the carbonyl group and the PPh$_3$ ligands. Chaudret and his co-workers [10] reported that the reactions of [RuClH(PPh$_3$)$_3$] with sodium methoxide and potassium t-butoxide yielded [RuH$_2$(CO)(PPh$_3$)$_3$] and [{RuH(OH)(PPh$_3$)$_2$(Bu^{t}OH)}$_2$], respectively, affording no stable alkoxoruthenium complex, whereas an ethoxo-ruthenium cluster complex [11] and several alkoxo complexes of the other VIII group metals have been reported [12, 13].



Scheme 1. (i) 2-Formylpyridine at room temperature. (ii) In refluxing benzene.

The ^{1}H NMR spectrum of II showed a characteristic AB type quartet for the methylene protons [Table I]. The ^{31}P{^{1}H} NMR spectrum of II in CH$_2$Cl$_2$ showed an AB pattern at 37.28 and 44.88 ppm [$^2J(P_AP_B)$ = 5 Hz] to lower field from 85% H$_3$PO$_4$ as an external reference. The ^{13}C{^{1}H} NMR spectrum of II in CD$_2$Cl$_2$ exhibited six singlets which were ascribed to (2-pyridyl)methoxo-N,O group, referring to the data of 2-picoline [14] and pyridine-coordinated complexes [15]; one methylene carbon at δ 74.5, one quarternary carbon at δ 171.8 (2-C), and four tertiary carbons at δ 122.6 (3-C), 136.0 (4-C), 119.3 (5-C), and 150.6 (6-C). Coupling with 31-phosphorus atoms was not observed for each of these carbon resonances. These data indicate that the two methylene protons are located at different chemical circumstances, and that the two PPh_3 ligands are situated at *cis* positions to each other (Scheme 1).

Complex II was converted into III in refluxing benzene, whereas III was also obtained directly by the reaction of I with 2-formylpyridine in refluxing benzene. The ^1H NMR spectrum of III showed a singlet at δ 4.81 for the methylene proton resonance, implying the equivalence of the two methylene protons and the *trans* coordination of the two PPh_3 ligands (Scheme). Another configuration of III, where pyridyl nitrogen is situated *trans* to chloro ligand, looks unlikely, since stabilization due to a push-pull effect between the donating pyridyl nitrogen and a π-accepting carbonyl ligand is not operative for this configuration.

The *cis*-form II, which was produced at room temperature, underwent the rearrangement at higher temperature to be converted into the *trans*-typed geometrical isomer, III. Accordingly, II is a kinetically favored complex and an intermediate from I to a thermodynamically stable complex III. As for III, a steric interaction between the two relatively bulky PPh_3 ligands is released, and the stabilization due to the push-pull effect is operative. Similar rearrangements have been also reported as for $[M(S_2CH)X(CO)(PPh_3)_2]$ (M = Ru and Os, X = Cl, Br or $OCOCF_3$) [2] and $[\mathrm{OsCl(PhN}\stackrel{\cdot\cdot}{-}\mathrm{CH}\stackrel{\cdot\cdot}{-}\mathrm{S)(CO)(PPh_3)_2}]$ [3]. Complexes IV and V were yielded only at high temperature and were ascribed to the *trans* form, where two PPh_3 ligands were located at *trans* positions to each other.

It has been reported that aldehydes and ketones are hydrogenated catalytically by transition metal complexes [16, 17]. Goetz and Orchin [16] proposed a mechanism for the catalytic hydrogenations, where aldehyde is inserted into a hydrido–metal bond to yield an active intermediate (an alkoxo–metal complex) which is converted into an alcohol and the initial hydrido–metal bond. Complexes II–V are the first stable alkoxo complexes of group VIII metals that were derived from the insertion reaction of organic carbonyl compounds into the hydrido–metal bond, and may be regarded as the stable models for the intermediate of the catalytic hydrogenation of the organic carbonyl compounds. It has been reported that $[Zr(\eta^5\text{-}C_5H_5)_2H_2]$ reacted with acetone to afford $[Zr(\eta^5\text{-}C_5H_5)_2(OCHMe_2)_2]$ [18].

It is noteworthy that 2-formylpyridine, one of aldehyde, reacted with I to give the insertion products II and III, but did not undergo the Tischenko type reaction, in sharp contrast with aliphatic aldehydes and benzaldehyde [7]. It seems likely that 2-formylpyridine is susceptible to hydrido shift to the formyl carbon *via* the coordination of the pyridyl group, rather than to the oxidative addition of aldehyde to a ruthenium complex [7].

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