

ORGANORUTHENIUM(II) COMPLEXES PRODUCED BY INSERTION REACTIONS OF  
SUBSTITUTED OLEFINS INTO A HYDRIDO-RUTHENIUM BOND

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Dimethyl fumarate, 2-vinylpyridine, and acrylonitrile insert into a H-Ru bond of  $[\text{RuClH}(\text{CO})(\text{PPh}_3)_3]$  (1) to yield new substituted alkyl-ruthenium(II) complexes. Methyl sorbate also reacted with 1 to give a new substituted  $\eta^3$ -allylruthenium(II) complex.

Insertion reactions of olefins into a hydrido-ruthenium (H-Ru) bond have been regarded as a fundamental and indispensable process in catalytic hydrogenations,<sup>1)</sup> isomerizations,<sup>2)</sup> hydrodimerization,<sup>3)</sup> and polymerizations<sup>4)</sup> with ruthenium complexes. It has been reported that  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{H}(\text{PPh}_3)_2]$  reacted with disubstituted acetylenes and a highly electron-deficient olefin,  $(\text{CF}_3)_2\text{C}=\text{C}(\text{CN})_2$  to afford insertion products.<sup>5)</sup> However, little has been known about stable ruthenium(II) complexes produced by the insertion reactions of olefinic compounds into the H-Ru bond.<sup>5)</sup> Komiya and Yamamoto investigated the reactions of  $[\text{RuH}_2(\text{PPh}_3)_4]$  with many olefinic compounds and obtained  $[\text{Ru}(\text{CH}_2=\text{CHR})(\text{PPh}_3)_3]$ ,<sup>6)</sup>  $[\text{RuH}(\text{OAc})(\text{PPh}_3)_3]$ ,<sup>7)</sup> and  $[\text{Ru}\{\text{CH}=\text{CMe}(\text{CO}_2\text{R}')\text{-}1\text{-}c,\text{ }o\}\text{H}(\text{PPh}_3)_3]$ .<sup>8)</sup> It is interesting to investigate the reactivities of  $[\text{RuClH}(\text{CO})(\text{PPh}_3)_3]$  (1) towards the olefinic compounds in comparison with those hydridoruthenium complexes. In this letter, we present some new organoruthenium(II) complexes obtained by the insertion reactions of a few substituted olefins into the H-Ru bond of 1.

A THF suspension (60 ml) containing 1 (1 mmol) and dimethyl fumarate (5 mmol) was stirred at room temperature for 20 h to yield a dark-green solution. The solution was concentrated and diluted with hexane. Dark green solids precipitated and was washed with hexane to give  $[\text{Ru}\{\text{CH}(\text{CO}_2\text{Me})\text{CH}_2\text{CO}_2\text{Me}\text{-}1\text{-}c,\text{ }2\text{-}o\}\text{Cl}(\text{CO})(\text{PPh}_3)_2]$  (2). Complex 1 reacted similarly with 2-vinylpyridine, methyl sorbate, and acrylonitrile to afford  $[\text{Ru}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4\text{N}\text{-}1\text{-}c,\text{ }M)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$  (3),  $[\text{Ru}\{\text{CH}(\text{CO}_2\text{Me})\text{CH}=\text{CHC}_2\text{H}_5\text{-}1\text{-}3\text{-}\eta^3\}\text{Cl}(\text{CO})(\text{PPh}_3)_2]$  (4), and  $[\{\text{Ru}(\text{CHMeCN})\text{Cl}(\text{CO})(\text{PPh}_3)_2\}_2]$  (5), respectively. Complex 5 reacted with 4-picoline (pic) in THF at room temperature, giving  $[\{\text{Ru}(\text{CHMeCN})\text{Cl}(\text{CO})(\text{pic})\text{-}(\text{PPh}_3)\}_2]$  (6). Complex 5 was sparingly soluble in usual organic solvents.

Table 1 summarizes the yields and some properties of the new organoruthenium(II) complexes 2-6.<sup>9)</sup> These complexes are air-stable in the solid state. The IR spectra of 2-6 lacked a  $\nu(\text{H-Ru})$  band near  $2000\text{ cm}^{-1}$ , which had been observed in the starting complex, 1, and showed a strong terminal metal-bonded  $\nu(\text{C}=\text{O})$  band in the region of  $1908\text{-}1940\text{ cm}^{-1}$ , whereas the band of 2 was accompanied by a weak band at  $1970\text{ cm}^{-1}$ .

The IR spectrum of 2 exhibited two bands at  $1660$  and  $1665\text{ cm}^{-1}$ , ascribable to two free ester carbonyl groups, and two bands at  $1621$  and  $1630\text{ cm}^{-1}$ , attributable to two coordinated ester carbonyl ones (Table 1). Similar coordination of ester car-

Table 1. Yields and some properties of the organoruthenium(II) complexes

Complex	Yield <sup>a)</sup> %	Mp <sup>b)</sup> °C	Color	IR data <sup>c)</sup>		<sup>1</sup> H-NMR data of CH <sub>3</sub> <sup>d)</sup>	
				ν(C≡O)	ν(C=O)	δ/ppm	
2	78	172-179	Yellowish green	1923s 1970w	1621s,1630sh 1660s,1665s	2.70(0.5H), 3.18(2.5H) 3.36(0.5H), 3.46(2.5H) <sup>e)</sup>	
3	57	170	Greenish gray	1908s	-	-	
4	32	94-96	Yellow	1940s	1698s	0.93(3H) <sup>f)</sup> , 3.09(3H)	
5	83	151-157	Greenish gray	1920s	-	-	
6	58 <sup>g)</sup>	165-171	Pale green	1940s	-	2.26(1.5H) <sup>h)</sup> , 2.37(1.5H) <sup>h)</sup> 0.23(1.5H) <sup>i)</sup> , 0.36(1.5H) <sup>e,i)</sup>	

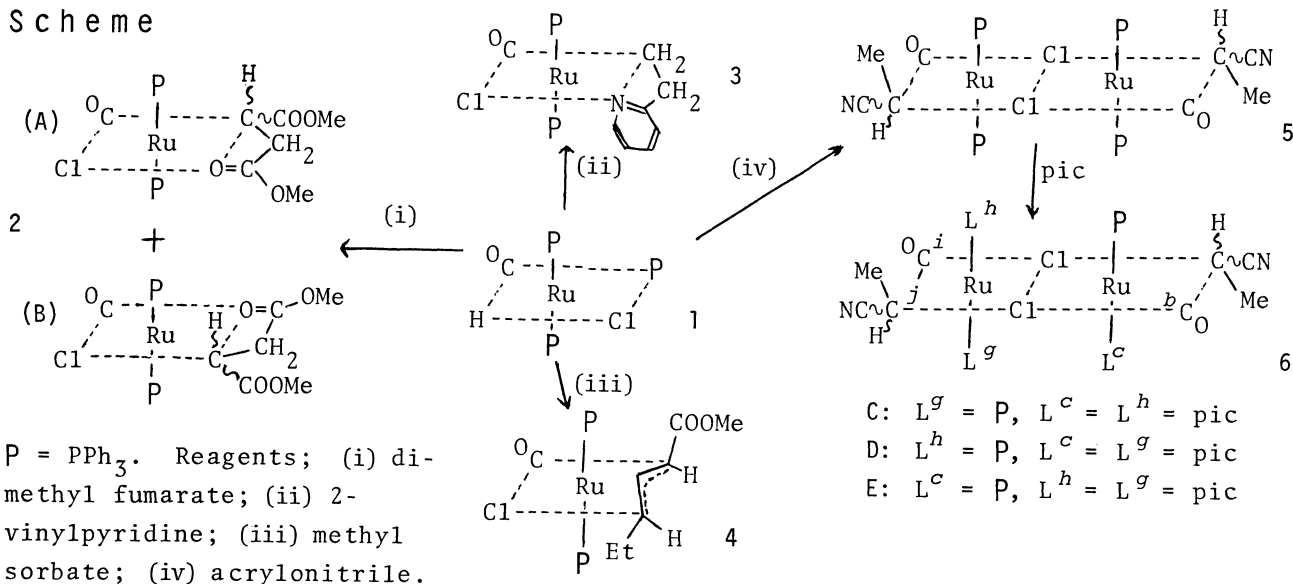
a) Based on 1, except 6. b) With decomposition. c) In cm<sup>-1</sup> in KBr disk. d) Singlet due to the ester methyl protons, in CDCl<sub>3</sub>, unless noted elsewhere. Approximate proton number is given in parentheses. e) In CD<sub>2</sub>Cl<sub>2</sub>. f) Triplet (<sup>3</sup>J<sub>HH</sub>=ca. 7 Hz) due to the methyl protons of the 1-3-η<sup>3</sup>-2-pentenyl group. g) Based on 5. h) Singlet due to the 4-picoline methyl protons. i) Doublet (<sup>3</sup>J<sub>HH</sub>=ca. 8 Hz) due to the methyl protons of the 1-cyanoethyl moiety.

bonyl group has been reported as for several ruthenium complexes.<sup>5,8,10)</sup> The <sup>1</sup>H-NMR spectrum of 2 showed three complicated resonances near δ 1.8 (ca. 0.8H), 2.8 (ca. 0.2H), and 3.7 (2H), in addition to four ester-methyl proton resonances (Table 1). The former two resonances were assignable to two kinds of 1-methine proton and the third one was to 2-methylene protons. In the <sup>1</sup>H-decoupled <sup>13</sup>C-NMR spectrum of 2 in CDCl<sub>3</sub>, eight singlets were detected in the range of δ 0-100 and classified as two sets; one set consisted of four relatively large signals at δ 25.6 (Me), 39.5 (Me), 49.7 (1-CH), and 53.8 (2-CH<sub>2</sub>); and the other consisted of four relatively small ones at δ 30.5 (Me), 33.0 (Me), 68.0 (2-CH<sub>2</sub>), and 98.6 (1-CH). These facts indicate unambiguously that 2 is composed of two geometrical isomers, and that each of the geometrical isomers involves a 1,2-bis(methoxycarbonyl)ethyl moiety, which is formed by the insertion reaction of dimethyl fumarate into the H-Ru bond of 1 and serves as a bidentate chelate coordinated with 1-methine carbon and 2-carbonyl oxygen to the ruthenium atom.

Since the 1-methine carbons in 2 showed neither doublet nor double doublet, the 1-methine groups were ascribed to a *cis*-position to two PPh<sub>3</sub> ligands. The two PPh<sub>3</sub> ligands are possibly situated *trans* to each other owing to their bulkiness, on the analogy of related organoruthenium(II) complexes.<sup>8,11,12)</sup> The metal-bonded carbonyl group is well known to exert a considerably strong deshielding effect upon the *trans*-situated ligand, owing to its π-back-bonding character. Accordingly, the major isomer was assigned to 2A, in which the ester carbonyl corresponding to the lowest-field methyl carbon resonance is located at the *trans* position to the metal-bonded carbonyl, whereas the minor isomer exhibiting the low-field 1-methine carbon resonance is analogically assigned to 2B.

The <sup>1</sup>H-NMR spectrum of 3 in CDCl<sub>3</sub> showed two multiplets near δ 1.8 (2H) and 2.6 (2H), indicating the presence of a 2-(2'-pyridyl)ethyl moiety. This was confirmed by the <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum in CDCl<sub>3</sub>, which afforded four singlets at δ 13.5 (1-CH<sub>2</sub>), 42.5 (2-CH<sub>2</sub>), 151.2 (6'-C of the pyridine ring), and 166.9 (2'-C). Complex 3 showed a low ν(C=O) band at 1908 cm<sup>-1</sup>. Similar low stretching frequencies of carbonyl group

## Scheme



were also observed for  $[\text{RuCl}_2(\text{CO})(\text{pyridine})_3]^{13)}$  and  $[\text{Ru}(\text{azb})(\text{Pz}_3\text{BH})(\text{CO})]$  (Hazb = azobenzene and Pz = 1-pyrazolyl)<sup>14)</sup> possessing the carbonyl group *trans* to a nitrogen donor ligand, and can be associated with the decrease of the bond order due to the strengthened  $\pi$ -back donation. On the basis of the low  $\nu(\text{C}=\text{O})$  frequency of the carbonyl group and of the relatively high-field resonances of the 1-methylene protons and carbon in 3, the pyridine-nitrogen and the 1-methylene group were ascribed to *trans* positions to the carbonyl group and the chloro ligand, respectively (Scheme).

The IR spectrum of 4 exhibited a strong  $\nu(\text{C}=\text{O})$  band at  $1698\text{ cm}^{-1}$ , assignable to a free ester carbonyl group. In the  $^1\text{H-NMR}$  spectrum of 4, the ester-methyl protons resonated as a sharp singlet at  $\delta$  3.09, indicating that 4 was actually a single component. A triplet at  $\delta$  0.93 was attributed to the methyl group possessing an adjacent methylene one (Table 1). A doublet at  $\delta$  2.02 (1H,  $^3J_{\text{HH}} = \text{ca. } 10\text{ Hz}$ ) and a triplet at  $\delta$  5.62 (1H) coupled to each other, and were ascribed to 1-methylene proton and an olefinic 2-proton in a substituted allyl group, respectively. The 3-proton resonance was absent in the region of  $\delta$  1.5-6.8 and was believed to be obscured by the phenyl proton ones. The large chemical shift difference between 1-H and 3-H was associated with a gap of the characters between the 1-methine group and the 3-methine one, caused both by the different substituents attached to the groups and by the different ligands situated *trans* to the groups. From these evidences, it is deduced that methyl sorbate inserted into the H-Ru bond of 1 to form a 1-(methoxycarbonyl)-1-3- $\eta^3$ -2-pent-enyl moiety.

The IR spectra of 5 and 6 showed a medium  $\nu(\text{C}\equiv\text{N})$  band at  $2200\text{ cm}^{-1}$ , attributable to an uncoordinated nitrile group. The elemental analyses of these two complexes imply that both 5 and 6 have one chlorine atom and four other coordination sites per ruthenium atom, indicating a chloro-bridged dinuclear structure (Scheme).<sup>11)</sup> Indeed, chlorine atoms have been reported to serve as bridge-forming ligands in many chloro-ruthenium(II) complexes.<sup>11,14)</sup> The single intensive  $\nu(\text{C}=\text{O})$  band of 5 or 6 suggests that the two carbonyl groups in the dinuclear structure are coordinated in an inversion symmetry (a *bi* type in Scheme) rather than in a  $\text{C}_2$  rotational symmetry around the Cl-Cl axis (a *bj* type).

It is worth noting that 4-picoline gives rise to the replacement of two  $\text{PPh}_3$  ligands in 5 instead of the splitting of the chloro bridge,<sup>11)</sup> to afford 6 with C-, D-, and/or E-type structures due to coordination position isomerism (Scheme). The steric interaction between two one-sided  $\text{PPh}_3$  ligands in the dinuclear structure is responsible for the replacement, and presumably rules out the D-type structure. It seems that the E-type structure is also unfavourable, since the second  $\text{PPh}_3$  ligand coordinated to the ruthenium atom is insusceptible to the replacement by 4-picoline, owing to the considerably strong *trans* influence of  $\text{PPh}_3$ .

The  $^1\text{H}$ -NMR spectrum of 6 exhibited two picoline-methyl resonances and two doublets assignable to the methyl protons of the 1-cyanoethyl moiety (Table 1). The  $^{31}\text{P}$ - $\{^1\text{H}\}$ -NMR spectrum of 6 in  $\text{CH}_2\text{Cl}_2$  showed four singlets of a virtually equal intensity at 89.13, 89.25, 95.82, and 95.91 ppm from trimethyl phosphite as the external reference. The data suggest that 6 consists of diastereomers of the C-type structure containing the two asymmetric 1-carbons of the 1-cyanoethyl moieties.

In conclusion, it is significantly noteworthy that the olefinic compounds investigated in the present study insert easily into the H-Ru bond of 1 to form the new stable organoruthenium(II) complexes, in sharp contrast with  $[\text{RuH}_2(\text{PPh}_3)_4]$ ,<sup>4,6-8)</sup> and that the hydride atom transfers to the  $\alpha$ -position of the olefins containing the coordinating substituent, such as the ester group or the pyridyl one, and does to the  $\beta$ -position of the  $\alpha,\beta$ -unsaturated nitrile. The ruthenium-carbon bonds formed by the insertion reactions are possibly stabilized by the coordination of the properly donating and  $\pi$ -accepting ligands, such as tertiary phosphine and carbonyl, and in some cases, by the electron-attracting group attached to the 1-carbon (2, and 4-6), by the chelate structure (2 and 3), or by the substituted  $\eta^3$ -allylic one (4).

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