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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 [RuClH(CO)$(PPh_3)_3$] (1) to yield new substituted alkylruthenium(II) complexes. Methyl sorbate also reacted with 1 to give a new substituted η^3-allylruthenium(II) complex.

Insertion reactions of oleins into a hydrido-ruthenium (H-Ru) bond have been regarded as a foundamental and indispensable process in catalytic hydrogenations,[1)] isomerizations,[2)] hydrodimerization,[3)] and polymerizations[4)] with ruthenium complexes. It has been reported that [Ru(η^5-C_5H_5)H$(PPh_3)_2$] reacted with disubstituted acetylenes and a highly electron-deficient olefin, $(CF_3)_2C=C(CN)_2$ to afford insertion products.[5)] However, little has been known about stable ruthenium(II) complexes produced by the insertion reactions of olefinic compounds into the H-Ru bond.[5)] Komiya and Yamamoto investigated the reactions of [$RuH_2(PPh_3)_4$] with many olefinic compounds and obtained [Ru(CH_2=CHR)$(PPh_3)_3$],[6)] [RuH(OAc)$(PPh_3)_3$],[7)] and [Ru{CH=CMe(CO_2R')-1-*c*,*o*}H$(PPh_3)_3$].[8)] It is interesting to investigate the reactivities of [RuClH(CO)$(PPh_3)_3$] (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 [Ru{CH(CO_2Me)CH_2CO_2Me-1-*c*,2-*o*}Cl(CO)$(PPh_3)_2$] (2). Complex 1 reacted similarly with 2-vinylpyridine, methyl sorbate, and acrylonitrile to afford [Ru($CH_2CH_2C_5H_4$N-1-*c*,*N*)Cl(CO)$(PPh_3)_2$] (3), [Ru{CH(CO_2Me)CH=CHC_2H_5-1-3-η^3}Cl(CO)-$(PPh_3)_2$] (4), and [{Ru(CHMeCN)Cl(CO)$(PPh_3)_2$}$_2$] (5), respectively. Complex 5 reacted with 4-picoline (pic) in THF at room temperature, giving [{Ru(CHMeCN)Cl(CO)(pic)-(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.[9)] These complexes are air-stable in the solid state. The IR spectra of 2-6 lacked a ν(H-Ru) band near 2000 cm^{-1}, which had been observed in the starting complex, 1, and showed a strong terminal metal-bonded ν(C≡O) band in the region of 1908-1940 cm^{-1}, whereas the band of 2 was accompanied by a weak band at 1970 cm^{-1}.

The IR spectrum of 2 exhibited two bands at 1660 and 1665 cm^{-1}, ascribable to two free ester carbonyl groups, and two bands at 1621 and 1630 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[a)] %	Mp[b)] °C	Color	IR data[c)] ν(C≡O)	IR data[c)] ν(C=O)	^{1}H-NMR data of CH_3[d)] 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)[e)]
3	57	170	Greenish gray	1908s	-	-
4	32	94-96	Yellow	1940s	1698s	0.93(3H)[f)], 3.09(3H)
5	83	151-157	Greenish gray	1920s	-	-
6	58[g)]	165-171	Pale green	1940s	-	2.26(1.5H)[h)], 2.37(1.5H)[h)] 0.23(1.5H)[i)], 0.36(1.5H)[e,i)]

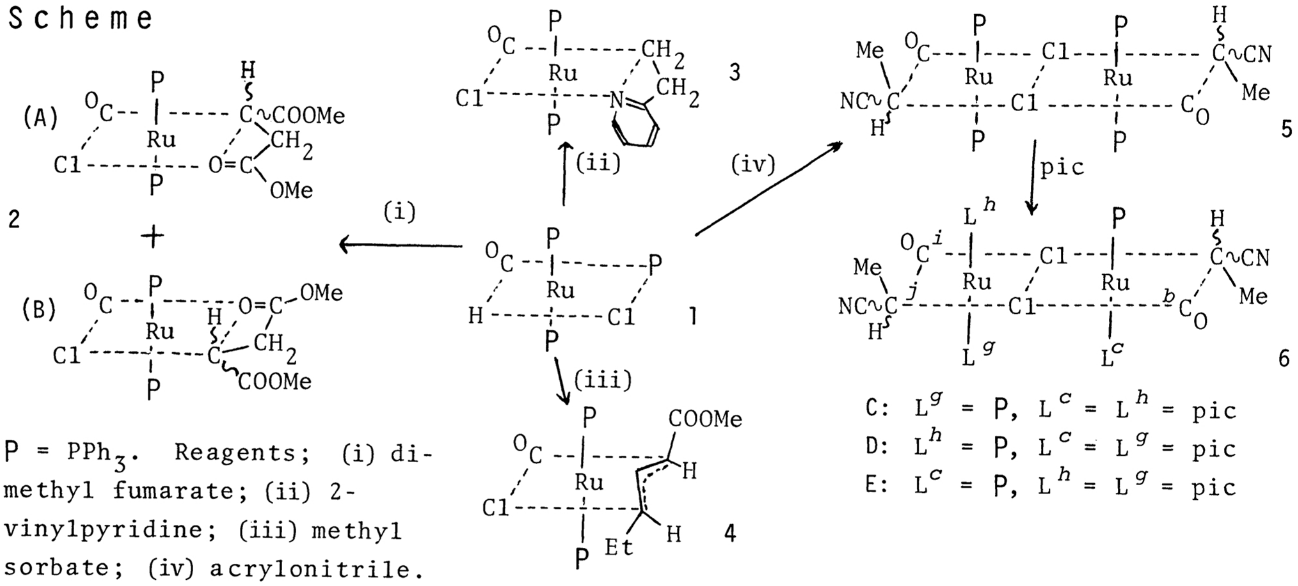
a) Based on 1, except 6. b) With decomposition. c) In cm^{-1} in KBr disk. d) Singlet due to the ester methyl protons, in $CDCl_3$, unless noted elsewhere. Approximate proton number is given in parentheses. e) In CD_2Cl_2. f) Triplet ($^3J_{HH}$=ca. 7 Hz) due to the methyl protons of the 1-3-η^3-2-pentenyl group. g) Based on 5. h) Singlet due to the 4-picoline methyl protons. i) Doublet ($^3J_{HH}$=ca. 8 Hz) due to the methyl protons of the 1-cyanoethyl moiety.

bonyl group has been reported as for several ruthenium complexes.[5,8,10)] The ^{1}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 ^{1}H-decoupled ^{13}C-NMR spectrum of 2 in $CDCl_3$, 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-$\underline{C}$H), and 53.8 (2-$\underline{C}H_2$); and the other consisted of four relatively small ones at δ 30.5 (Me), 33.0 (Me), 68.0 (2-$\underline{C}H_2$), and 98.6 (1-$\underline{C}$H). 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_3 ligands. The two PPh_3 ligands are possibly situated *trans* to each other owing to their bulkiness, on the analogy of related organoruthenium(II) complexes.[8,11,12)] 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 ^{1}H-NMR spectrum of 3 in $CDCl_3$ 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 $^{13}C\{^1H\}$-NMR spectrum in $CDCl_3$, which afforded four singlets at δ 13.5 (1-$\underline{C}H_2$), 42.5 (2-$\underline{C}H_2$), 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^{-1}. Similar low stretching frequencies of carbonyl group

Scheme



P = PPh_3. Reagents; (i) dimethyl fumarate; (ii) 2-vinylpyridine; (iii) methyl sorbate; (iv) acrylonitrile.

C: L^g = P, L^c = L^h = pic
D: L^h = P, L^c = L^g = pic
E: L^c = P, L^h = L^g = pic

were also observed for $[RuCl_2(CO)(pyridine)_3]$ 13) and $[Ru(azb)(Pz_3BH)(CO)]$ (Hazb = azobenzene and Pz = 1-pyrazolyl) 14) 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 π-back donation. On the basis of the low ν(C≡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 ν(C=O) band at 1698 cm^{-1}, assignable to a free ester carbonyl group. In the ^1H-NMR spectrum of 4, the ester-methyl protons resonated as a sharp singlet at δ 3.09, indicating that 4 was actually a single component. A triplet at δ 0.93 was attributed to the methyl group possessing an adjacent methylene one (Table 1). A doublet at δ 2.02 (1H, $^3J_{HH}$=ca. 10 Hz) and a triplet at δ 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 δ 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-η^3-2-pentenyl moiety.

The IR spectra of 5 and 6 showed a medium ν(C≡N) band at 2200 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). 11) Indeed, chlorine atoms have been reported to serve as bridge-forming ligands in many chlororuthenium(II) complexes. 11,14) The single intensive ν(C≡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 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 PPh_3 ligands in 5 instead of the splitting of the chloro bridge,[11] to afford 6 with C-, D-, and/or E-type structures due to coordination position isomerism (Scheme). The steric interaction between two one-sided 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 PPh_3 ligand coordinated to the ruthenium atom is insusceptible to the replacement by 4-picoline, owing to the considerably strong *trans* influence of PPh_3.

The ^1H-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 $^{31}P\text{-}\{^1H\}$-NMR spectrum of 6 in CH_2Cl_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 $[RuH_2(PPh_3)_4]$,[4,6-8] and that the hydride atom transfers to the α-position of the olefins containing the coordinating substituent, such as the ester group or the pyridyl one, and does to the β-position of the α,β-unsaturated nitrile. The ruthenium-carbon bonds formed by the insertion reactions are possibly stabilized by the coordination of the properly donating and π-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 η^3-allylic one (4).

References and Note

1) C. A. Tolman, "Transition Metal Hydrides", Ed. by E. L. Muetterties, Marcel Dekker, Inc., New York, 1971, pp. 271-312, and literatures cited therein.
2) R. A. Shunn, *Inorg. Chem.*, 9, 2567 (1970).
3) A. Misono, Y. Uchida, M. Hidai, I. Inomata, Y. Watanabe, and M. Takeda, *Kogyo Kagaku Zasshi*, 72, 1801 (1969).
4) S. Komiya, A. Yamamoto, and S. Ikeda, *Bull. Chem. Soc. Jpn.*, 48, 101 (1975).
5) T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1974, 106.
6) S. Komiya and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 49, 2553 (1976).
7) S. Komiya and A. Yamamoto, *J. Organomet. Chem.*, 87, 333 (1975).
8) S. Komiya and A. Yamamoto, *J. Chem. Soc., Chem. Commun.*, 1975, 475. S. Komiya, T. Ito, M. Cowie, A. Yamamoto, and J. A. Ibers, *J. Am. Chem. Soc.*, 98, 3874 (1976).
9) The elemental analyses of 2-6 are satisfactory.
10) G. Sbrana, G. Braca, and E. Benedetti, *J. Chem. Soc., Dalton Trans.*, 1975, 754.
11) K. Hiraki, Y. Obayashi, and Y. Oki, *Bull. Chem. Soc. Jpn.*, 52, 1372 (1979).
12) P. B. Hitchcock, M. F. Lappert, and P. L. Pye, *J. Chem. Soc., Chem. Commun.*, 1977, 196.
13) S. D. Robinson and G. Wilkinson, *J. Chem. Soc., A*, 1966, 300.
14) M. I. Bruce, M. Z. Iqbal, and F. G. A. Stone, *J. Chem. Soc., A*, 1971, 2820.

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