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Oxidative Addition of Vinyl Acetate to Ruthenium(0) Involving Carbon Oxygen Bond Cleavage Forming a Novel Vinyl(acetato)tris(triethylphosphine)ruthenium(II)

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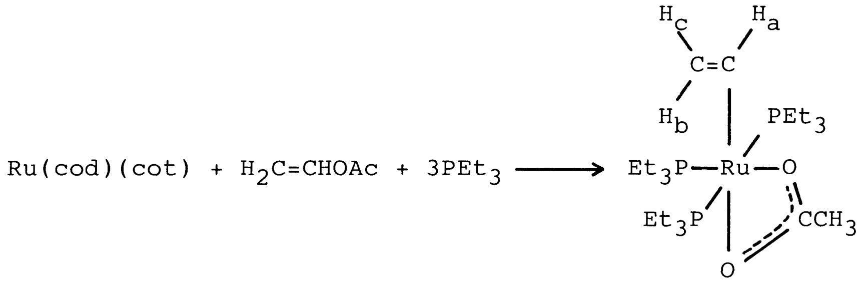
Vinyl acetate oxidatively adds to (1,5-cyclooctadiene)(1,3,5-cyclooctatriene)ruthenium(0) in the presence of triethylphosphine to give mer-vinyl(acetato)tris(triethylphosphine)ruthnium(II) at 50 °C in hexane, which has been unequivocally characterized by ^{1}H, ^{31}P, and ^{13}C NMR, IR, elemental analysis, and X-ray structure analysis.

Oxidative addition of allyl carboxylates involving carbon-oxygen bond cleavage to the low valent transition metal complexes to give π-allyl intermediates is often postulated in the various organic reactions promoted by transition metal complexes.1) Evidence of such an oxidative addition has been recently demonstrated by isolating the intermediate π-allyl metal species in the reaction of zero-valent nickel or palladium complexes in the presence of suitable phosphine ligands by Yamamoto et al.2) The results elegantly support the involvement of oxidative addition process in these reactions. However, the examples of oxidative addition of vinylic carboxylates involving carbon-oxygen bond cleavage have not been known so far probably because of the instability of the reaction product. We now report the first example of the isolation of vinyl(acetato)tris(triphenylphosphine)ruthenium(II) by the oxidative addition of vinyl acetate to ruthenium(0) complex.

Reaction of (1,5-cyclooctadiene)(1,3,5-cyclooctatriene)ruthenium(0)3) with vinyl acetate in the presence of 3 equivalents of triethylphosphine ligand in hexane at 50 °C for 12 h gave yellow homogeneous solution accompanied by evolution of a small amount of ethylene. The yellow solid, **1**, obtained after evaporation of all volatile materials, was purified by passing through 20 cm neutral alumina columm followed by recrystallization. The complex was unequivocally characterized as mer-vinyl(acetato)tris(triethylphosphine)ruthenium(II), **1**, by ^1H, ^{31}P, and ^{13}C NMR, IR, elemental analysis,and X-ray structure analysis as well as by chemical reactions.[4] Yield 33%. Mp 73-75 °C.



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The ^{31}P NMR of **1** shows a triplet and a doublet in a 2:1 ratio at 46.5 and 14.6 ppm, indicating the existence of two magnetically equivalent phosphorus nuclei and one unique phosphorous nucleus. In the ^1H NMR of **1**, signals due to vinylic protons appeared at 8.52 ppm as a double double quartet and at 6.06 and 5.38 ppm as double quartets, respectively. All the vinylic protons have the coupling with three phosphorus nuclei in addition to coupling with each other, suggesting that the vinylic entity is placed in a cis position to the three triethylphosphine ligands. Such long range spin-spin coupling may be occurred through π-electrons of vinyl group. One of the vinylic protons H_a is observed at relatively lower field. In the ^{13}C NMR of **1** the α-carbon signal in the vinyl group also resonates as a quartet at fairly low field (163.2 ppm), whereas the β-carbon one appears as a singlet at 119.1 ppm. These unusual low field shifts may be due to a strong anisotoropy of the adjacent ruthenium metal. Similar low field chemical shift has been observed in some vinyl transition metal complexes.[5] The IR spectrum of **1** shows ν(OCO) bands at 1538 and 1435 cm^{-1}. The moderate value of the difference between two bands(103 cm^{-1}) suggests the coordination of the acetato ligand as a bidentate ligand.[6]

Molecular structure of **1** determined by X-ray crystallography[7] is shown in Fig. 1. All the bond lengths and angles are quite normal and the observed meridional structure is consistent with the above spectroscopic data.

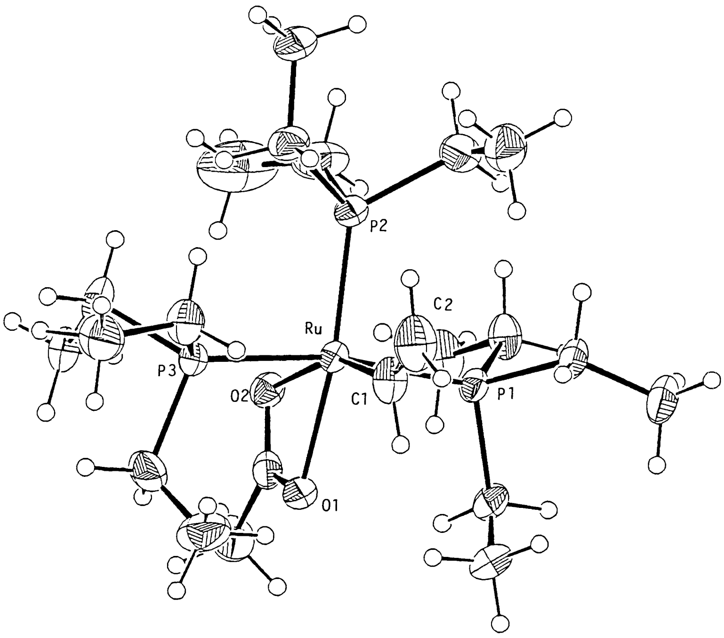

Fig. 1. Molecular structure of **1** .

Thermolysis of **1** in decalin at 75 °C for 10 h liberated ethylene in addition to small amounts of 1- and 2-butenes, and propylene. The proton source of ethylene evolved seem to be triethylphosphine or vinyl ligands, since thermolysis of **1** in C_6D_6 afforded only C_2H_4. Butenes evolved are considered to be formed by the dimerization of C_2 fragments, but the route for propylene formation is not clear at present.

$$\mathbf{1} \longrightarrow \underset{33\%}{C_2H_4} + \underset{18\%}{C_4H_8} + \underset{5\%}{C_3H_6}$$

Hydrogenolysis of **1** with molecular hydrogen was performed in benzene to give mainly ethylene. Small amount of ethane was also formed. Since the substantial amount of ethane was formed even in the initial stage of the reaction, ethylene and ethane are considered to be formed *via* independent reaction pathways. The ruthenium product is found to be hydrido(acetato)tris(triethylphosphine)ruthenium(II) by the ^{1}H NMR analysis.[8)]

$$\mathbf{1} + H_2 \longrightarrow \underset{75\%}{C_2H_4} + \underset{25\%}{C_2H_6}$$

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References

1) For example: R. F. Heck, "Organotransition Metal Chemistry," Academic Press, New York (1974); J. Tsuji, "Organic Synthesis by Means of Transition Metal Complexes," Springer-Verlag, West Berlin (1977); J. P. Collman and L. S. Hegedas, "Principles and Applications of Organotransition Metal Complexes," University Science Books, Mill Valley CA (1980) and references cited therein.

2) T. Yamamoto, O. Saito, and A. Yamamoto, J. Am. Chem. Soc., 103, 5600 (1981); T. Yamamoto, J. Ishizu and A. Yamamoto, ibid., 103, 6863 (1981); T. Yamamoto, M. Akimoto, O. Saito, and A. Yamamoto, Organometallics, 5, 1559 (1986).

3) P. Pertici and G. Vitulli, J. Chem. Soc, Dalton Trans., 1980, 1962.

4) Anal. Found: C, 48.81; H, 9.66%. Calcd for $C_{22}H_{51}O_2P_3Ru$: C, 48.79; H, 9.49%. ^1H NMR(in C_6D_6): 8.52 ppm (ddq, J(HH)=10.3, 17.6, J(HP)=2.4, 1H, Ru-C$\underline{H}$=); 6.06 (dq, J(HH)=10.3, J(HP)=2.4, 1H, =CH_2); 5.38 (dq, J(HH)=17.6, J(HP)=2.4, 1H, =CH_2); 1.85 (s, 3H, OAc); 1.5-2.0 (m, 18H, $P(C\underline{H}_2CH_3)_3$); 0.9-1.2 (m, 27H, $P(CH_2C\underline{H}_3)_3$). ^{31}P NMR(in C_6D_6, ppm from external PPh_3): 46.5 (t, J(PP)=32.9 Hz); 14.6 (d, J(PP)=32.9). ^{13}C NMR(in C_6D_6): 180.8 (s, $O\underline{C}OCH_3$); 163.2 (q, J(CP)=13.4, Ru-$\underline{C}$=); 119.1 (s, Ru-C=$\underline{C}$); 24.9 (s, $OCO\underline{C}H_3$); 23.2 (s, J(CP)=22.0, $P(\underline{C}H_2CH_3)_3$ trans to O); 17.5 (t, J(PP)=9.8, $P(\underline{C}H_2CH_3)_3$ trans to each other); 9.3 (d, J(CP)=3.7, $P(CH_2\underline{C}H_3)_3$ trans to O); 9.2 (s, $P(CH_2\underline{C}H_3)_3$ trans to each other).

5) S. Komiya, T. Ito, M. Cowie, A. Yamamoto, and J. A. Ibers, J. Am. Chem. Soc., 98, 3874 (1976); A. J. Deeming, S. Hasso, and M. Underhill, J. Chem. Soc., Dalton Trans., 1974, 1614; T. T. Wenzel and R. G. Bergman, J. Am. Chem. Soc., 108, 4856 (1985).

6) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3rd ed, John Wiley & Sons, New York(1977), p. 232.

7) Crystal data: monoclinic, space group $2_1/c$, a=17.518(2), b=11.063(2), c=15.019(2) Å, β=102.72(1)°, Z=4, Mo-K_α radiation, $2\Theta_{max}$=50.5°, heavy atom method, block-diagonal least squares procedure, final R value for 3902 reflections ($|F_o|>3(|F_o|)$) 0.052. Selected bond lengths and angles: Ru-C(1)=2.036(7), Ru-O(1)=2.229(4), Ru-P(1)=2.370(2), Ru-P(2)=2.247(2), Ru-P(3)=2.394(2), C(1)-C(2)=1.258(11) Å; Ru-C(1)-C(2)=142.8(6), C(1)-Ru-C(2)=99.7(3), C(1)-Ru-P(1)=87.98(11), C(1)-Ru-P(2)=97.48(19), C(1)-Ru-P(3)=87.47(19), O(1)-Ru-O(2)=57.21(14), P(1)-Ru-P(2)=95.01(6), P(2)-Ru-P(3)=96.58(6)°. Computations were carried out on an ACOS 850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

8) ^1H NMR(in C_6D_6): -22.0 (dt, J(HP)=24, 33, 1H, Ru-H), 1.89 (s, 3H, OAc), 0.9-2.0 (m, 45H, PEt_3). IR: ν(Ru-H)=1988, ν(OCO)=1554, 1439 cm^{-1}.

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