BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2935 (1972)

Preparation of Rhodium Acrolein Complexes

Masanobu Hidai, Kazuo Ishimi, Masa-aki Iwase, and Yasuzo Uchida
Department of Industrial Chemistry, The University of Tokyo, Hongo, Tokyo

(Received May 18, 1972)

Several acrolein complexes of nickel,[1] iron,[2] molybdenum,[3] and copper[4] have been known. We have now prepared rhodium acrolein complexes from acrolein and the rhodium(I) cyclooctene complex $[RhCl(C_8H_{14})_2]_2$.

Acrolein reacts smoothly with $[RhCl(C_8H_{14})_2]_2$ in toluene at −10°C under nitrogen and a brown complex formulated as $RhCl(CH_2{=}CHCHO)_2$ (I) was obtained in a high yield. Infrared spectroscopic evidence indicates the manner of attachment of acrolein to the metal atom. The C=C stretching frequency of acrolein is shifted about 13 cm^{-1} to the lower frequency side by the ligation. Two strong C=O stretching bands are observed at 1670 and 1545 cm^{-1}. The former band is very close to the aldehydic carbonyl absorption for the free ligand in the liquid state (1675 cm^{-1}). The latter band is 130 cm^{-1} lower than that of free acrolein. These indicate the presence of two types of coordinated acrolein ligands: One coordinates to the rhodium metal with both C=O and C=C groups, while the other coordinates with only the C=C bond.

The reaction of acrolein with $[RhCl(C_8H_{14})_2]_2$ at 30°C also yields a brown complex with the same empirical formula as the above complex in a high yield. However, the IR spectrum of the complex exhibites a sharp band at 2000 cm^{-1} and a weak band at 1740 cm^{-1} in addition to two bands at 1670 and 1545 cm^{-1} described above. The reaction of this complex with excess of triphenylphosphine yields a mixture of $RhCl(CO)(PPh_3)_2$ and $RhCl(PPh_3)_3$ in a ratio of about 4: 1 with evolution of ethylene. The band at 2000 cm^{-1} is, therefore, assigned to C≡O stretching vibration. Furthermore, the intensity of the band at 1670 cm^{-1} is weak compared with that of the complex obtained at −10°C, indicating that some of acrolein ligands coordinating to the metal *via* the C=C bond are converted into ethylene and carbon monoxide ligands and $RhCl(CO)(CH_2{=}CH_2)(CH_2{=}CHCHO)$ (II) is formed. On the other hand, the weak band at 1740 cm^{-1} in the keto-region may indicate the presence of a small amount of an acyl complex. From these results, it may be reasonable to conclude that the acrolein complex obtained at 30°C is a mixture of I, II, and an acyl complex.

$$[RhCl(C_8H_{14})_2]_2 + CH_2{=}CHCHO \longrightarrow \underset{\text{(I)}}{RhCl(CH_2{=}CHCHO)_2} + \underset{\text{(II)}}{RhCl(CO)(CH_2{=}CH_2)(CH_2{=}CHCHO)} + \text{Acyl complex}$$

These rhodium acrolein complexes are fairly air-stable. They are slightly soluble in tetrahydrofuran and scarcely soluble in benzene and ether. The thermal decomposition of the complexes occurs *in vacuo* above about 145° with evolution of ethylene and carbon monoxide, yielding $[RhCl(CO)_2]_2$. Numerous fruitless attempts were made to isolate the complex II and the acyl complex in a pure state.

Experimental

All reactions were carried out under a nitrogen atmosphere. The rhodium(I) cyclooctene complex $[RhCl(C_8H_{14})_2]_2$ was prepared by the published procedure.[5]

Reaction of Acrolein with $[RhCl(C_8H_{14})_2]_2$ *at −10°C.* To a stirred solution of $[RhCl(C_8H_{14})_2]_2$ (1.0 g) and toluene (80 m*l*) was added 2 m*l* of acrolein at 0°C. After stirring for 3 hr, a brown complex precipitated was washed with toluene and petroleum ether several times (0.38 g, 54% yield).

Found: C, 28.55; H, 3.40; O, 12.86; Cl, 14.46%. Calcd for $C_6H_8O_2ClRh$: C, 28.77; H, 3.22; O, 12.78; Cl, 14.15%.

Reaction of Acrolein with $[RhCl(C_8H_{14})_2]_2$ *at 30°C.* The procedure was the same as above, except that the reaction temperature was 30°C and the reaction time was 0.5 hr (0.40 g, 57% yield).

Found: C, 28.97; H, 3.38; O, 11.52; Cl, 14.60%. Calcd for $C_6H_8O_2ClRh$: C, 28.77; H, 3.22; O, 12.78; Cl, 14.15%.

---

[1] G. N. Schrauzer, *J. Amer. Chem. Soc.*, **81**, 5310 (1959); *Chem. Ber.*, **94**, 642 (1961).

[2] E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, **46**, 288 (1963).

[3] D. P. Tate, A. A. Buss, J. M. Augl, B. L. Ross, J. G. Grasselli, W. M. Ritchey, and F. J. Knoll, *Inorg. Chem.*, **4**, 1323 (1965).

[4] S. Kawaguchi and T. Ogura, *ibid.*, **5**, 844 (1966).

[5] L. Porri, A. Lionetti, G. Allegra, and A. Immirzi, *Chem. Commun.*, 336 (1965).