

Preparation of Rhodium Acrolein Complexes

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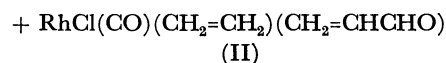
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Several acrolein complexes of nickel,¹⁾ iron,²⁾ molybdenum,³⁾ and copper⁴⁾ have been known. We have now prepared rhodium acrolein complexes from acrolein and the rhodium(I) cyclooctene complex $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$.

Acrolein reacts smoothly with $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$ in toluene at -10°C under nitrogen and a brown complex formulated as $\text{RhCl}(\text{CH}_2=\text{CHCHO})_2$ (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 $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$ 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 exhibits 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 $\text{RhCl}(\text{CO})\text{-(PPh}_3)_2$ and $\text{RhCl}(\text{PPh}_3)_3$ 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-

$(\text{CO})(\text{CH}_2=\text{CH}_2)(\text{CH}_2=\text{CHCHO})$ (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.



+ 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 $[\text{RhCl}(\text{CO})_2]_2$. 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 $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$ was prepared by the published procedure.⁵⁾

Reaction of Acrolein with $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$ at -10°C .

To a stirred solution of $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$ (1.0 g) and toluene (80 ml) was added 2 ml 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 $\text{C}_6\text{H}_8\text{O}_2\text{ClRh}$: C, 28.77; H, 3.22; O, 12.78; Cl, 14.15%.

Reaction of Acrolein with $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$ 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 $\text{C}_6\text{H}_8\text{O}_2\text{ClRh}$: C, 28.77; H, 3.22; O, 12.78; Cl, 14.15%.

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