

## Acrylonitrile Complexes of Ruthenium Chloride which Catalyze the Dimerization of Acrylonitrile to 1,4-Dicyanobut-1-ene

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RECENTLY we have found that acrylonitrile is converted into a mixture of propionitrile and 1,4-dicyanobut-1-ene by ruthenium trichloride trihydrate in alcohol under a hydrogen atmosphere. To elucidate the mechanism of this reaction, we have studied the reaction between  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  and acrylonitrile in ethanol or methanol, and isolated two yellow complexes which show interesting differences from the one obtained from rhodium trichloride<sup>1</sup> in structure and chemical nature.

The first complex was obtained by heating a solution of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  in ethanol (1 g. in 20 ml.) under reflux with a large excess (4 ml.) of acrylonitrile for 2 hr. under a nitrogen atmosphere. The complex is very soluble in  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ , soluble in MeOH and EtOH, and nearly insoluble in acetone and ether. It decomposes *in vacuo* above *ca.* 100° to give acrylonitrile, and its elemental analysis is in accord with the formula  $(\text{CH}_2:\text{CHCN})_3\text{-RuCl}_2$ .

Infrared-spectroscopic evidence indicates the manner of attachment of acrylonitrile to the metal atom. The complex shows  $\text{C}\equiv\text{N}$  stretching absorption at 2230  $\text{cm}^{-1}$  shifted to higher frequency from that in the free ligand (2214  $\text{cm}^{-1}$ ), and a weak unshifted  $\text{C}=\text{C}$  stretching absorption at 1600  $\text{cm}^{-1}$ . The shift to higher frequencies of the  $\text{C}\equiv\text{N}$  absorption is due to the predominance of

a kinematic effect<sup>2</sup> caused by bonding of the  $\text{C}\equiv\text{N}$  group through the nitrogen atom. Furthermore, the region 650—1500  $\text{cm}^{-1}$  is remarkably similar to the spectrum of pentacarbonylacrylonitriletungsten,<sup>3</sup> in which acrylonitrile is bonded to the metal through the nitrogen lone-pair.

Acrylonitrile is converted catalytically into a mixture of propionitrile and 1,4-dicyanobut-1-ene by the complex under a hydrogen atmosphere; the reaction does not, however, occur under a nitrogen atmosphere. Thus, when acrylonitrile was treated with a solution of the complex in ethanol (0.200 g. in 20 ml.) under 20 atm. of hydrogen for 1 hr. at 150° in a stainless steel autoclave, propionitrile (46%), adiponitrile (4%), and 1,4-dicyanobut-1-ene (*cis:trans* = 1:1.3) (50%) were obtained.

The second complex, which also catalyzes the dimerization of acrylonitrile under a hydrogen atmosphere, was obtained by the reaction of acrylonitrile and  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  in ethanol at 150° under a hydrogen atmosphere in an autoclave. The infrared spectrum of the complex shows two absorption peaks at *ca.* 2100 and 2200  $\text{cm}^{-1}$ . The complex decomposes *in vacuo* above *ca.* 100° to give propionitrile as well as acrylonitrile. This indicates the presence of a cyanoethyl group attached to the metal atom. Experiments are in progress to determine the structure of this complex.

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<sup>2</sup> D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Inorg. Nuclear Chem.*, 1961, **21**, 33.

<sup>3</sup> A. G. Massey, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1172.