

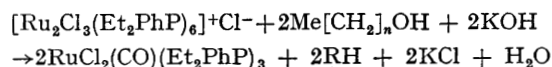
## Olefin Formation from Saturated Aldehydes and Acids by Reaction with Ruthenium and Rhodium Complexes

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THE abstraction of carbonyl groups from organic molecules by transition metals is well known, but the accompanying production of olefin has not been previously reported.

In examining the reaction of alcohols in the presence of base<sup>1,2</sup> with the complexes  $[\text{Ru}_2\text{Cl}_3(\text{Et}_2\text{PhP})_6]^+\text{Cl}^-$  (I),  $\text{RuCl}_3(\text{Et}_2\text{PhP})_3$  (II),  $\text{OsCl}_3(\text{Et}_2\text{PhP})_3$  (III), and  $\text{RhCl}_3(\text{Et}_2\text{PhP})_3$  (IV) we

observed that the formation of paraffin according to an equation<sup>2</sup> of the type

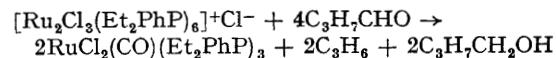


was accompanied, for alcohols with  $n > 1$ , by some of the corresponding olefin. Thus the reaction of (I) with n-propanol gave a little ethylene (< 10%), n-butanol a little propene and isopentanol some isobutene and some propene: (IV) with n-propanol gave  $40 \pm 10\%$  ethylene.

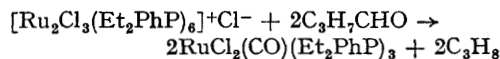
Reaction of (I) with ethanol in the presence of propionaldehyde led to ethylene formation, indicating that the aldehyde might be the source of the olefin.

We have now found that the complex  $[\text{Ru}_2\text{Cl}_3(\text{Et}_2\text{PhP})_6]^+\text{Cl}^- \cdot 2\text{MeOCH}_2\text{CH}_2\text{OH}$  reacts with n-butyraldehyde as solvent in the absence of base in an evacuated sealed tube or under nitrogen at 80°C for about 60 hrs. to give  $\text{RuCl}_2(\text{CO})(\text{Et}_2\text{PhP})_3$ . No hydrogen was formed during the reaction, and the principal volatile product was propene together with some propane. In one reaction the percentage of propene relative to propane determined by mass spectrometry was found to be  $93 \pm 5\%$  and in another  $80 \pm 5\%$ , the temperature conditions being slightly different. The hydrocarbon to ruthenium ratio was 1:1; n-butanol was detected as a further reaction product by vapour-phase chromatography.

It appears that olefin is produced according to the equation



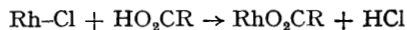
The propane probably results from the competing reaction



which is one of the stages in the mechanism of the decarbonylation of alcohols suggested by Chatt, Shaw, and Field<sup>2</sup>.

The first stage in the reaction of  $[\text{Ru}_2\text{Cl}_3(\text{Et}_2\text{PhP})_6]^+\text{Cl}^-$  with aldehyde is the formation of a diamagnetic rust-coloured complex which is a non-electrolyte in nitrobenzene. The compound analyses for  $[\text{RuCl}_2(\text{Et}_2\text{PhP})_3]_n$ . Molecular weights in dichloromethane give values of  $n$  between 1 and 2 indicating possibly a dissociating dimer. The same complex can be obtained by refluxing  $[\text{Ru}_2\text{Cl}_3(\text{Et}_2\text{PhP})_6]^+\text{Cl}^-$  with methyl acetate or diethyl ketone, but no further reaction occurs. Studies using RCDO are being used to elucidate the mechanism of this reaction particularly with regard to the formation of the alcohol.

We have also observed that when  $\text{RhCl}_3(\text{Et}_2\text{PhP})_3$  is heated under reflux with saturated carboxylic acids, olefins are again produced. Propionic acid gives ethylene, and hexanoic acid gives pent-2-ene, mass spectrometry indicating the absence of pentane in the latter case. The final complex is  $\text{RhCl}(\text{CO})(\text{Et}_2\text{PhP})_2$  but the stoichiometry appears complex since up to three molecules of olefin are formed per atom of rhodium. The first step appears to be formation of the carboxylato-complex



since one mole only of HCl is evolved per mole of starting complex.

(Received, February 7th, 1966; Com. 078.)

<sup>1</sup> J. Chatt and B. L. Shaw, *Chem. and Ind.*, 1960, 931; 1961, 290.

<sup>2</sup> J. Chatt, B. L. Shaw, and (in part) A. E. Field, *J. Chem. Soc.*, 1964, 3466.