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Homogeneous Pentyne Hydrogenation Catalysed by $H_4Ru_4(CO)_{12}$

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As part of our studies on the catalytic activity of metal-cluster compounds in the isomerisation and hydrogenation processes [1–4] we have examined the catalytic behaviour of $H_4Ru_4(CO)_{12}$ in the homogeneous hydrogenation of 1-pentyne and 2-pentyne. During these last years a number of metal-clusters have received attention and new catalytic processes have been investigated [5–8].

A toluene solution of $H_4Ru_4(CO)_{12}$, 0.37 m*M*, at 80.0 °C under H_2 at atmospheric pressure catalyzes the hydrogenation of 1-pentyne, 37 m*M*, to 1-pentene during the first steps of the reaction. The initial rate of hydrogenation is 2.2 m*M* h^{-1}, when the volume of the vial is 70 ml and the volume of the solution is 5 ml. Isomerisation of 1-pentene to 2-*cis*- and 2-*trans*-pentene follows and the *cis*/*trans* ratio falls down from 1 to 0.35 at the equilibrium. After completion of 1-pentyne hydrogenation, the pentenes are converted to pentane.

Addition of hydrogen to 2-pentyne under the same conditions leads to the production of 2-*cis*-pentene, which is the only pentene present during the reduction of the first 10% of 2-pentyne. The initial rate of hydrogenation is 3.3 m*M* h^{-1}, when the volumes of the vial and of the solution are identical to those reported for 1-pentyne. During the successive steps the isomerisation of 2-*cis*-pentene occurs, but the *cis*/*trans* ratio remains above unity till 45% of the 2-pentyne, which was originally present, is hydrogenated, as shown in the Figure. Also in this case hydrogenation to pentane follows.

Both pentynes readily react with $H_4Ru_4(CO)_{12}$ to give a number of substituted complexes which are at present only partially characterised. The presence of these complexes can be observed when the pentynes have been converted to pentenes to an extent of about 10%. The reaction mixture obtained after the complete reduction of the pentynes is still catalytically active towards the reduction of freshly added pentynes, although the initial hydrogenation rate is considerably decreased. Thus the most active species is $H_4Ru_4(CO)_{12}$, which is very likely to coordinate the organic substrate by cleavage of Ru–CO bonds. This is supported by the increase of the rate of hydro-

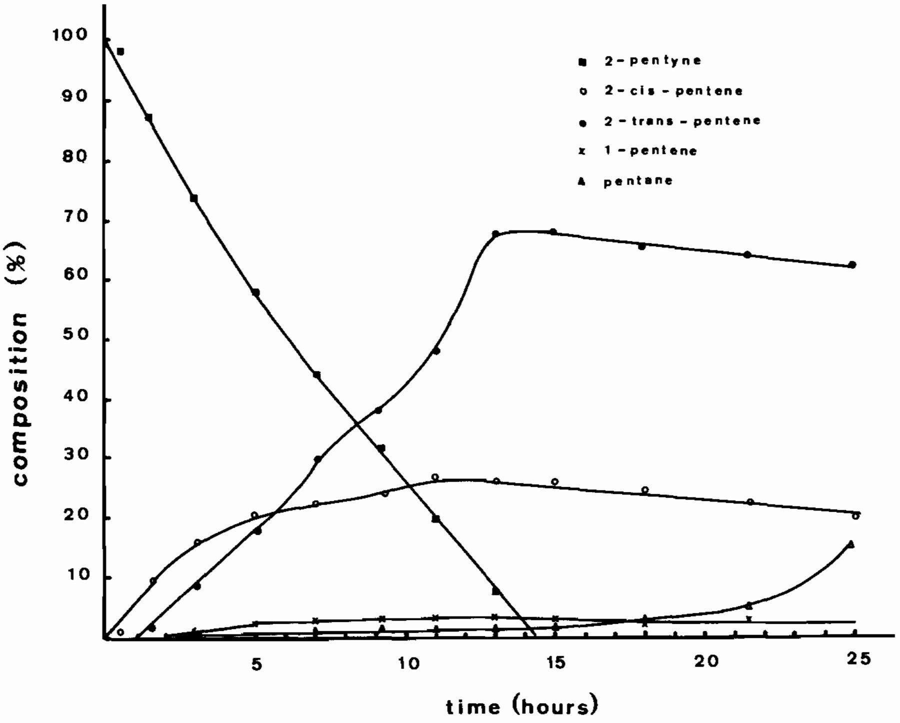

Figure. Hydrogenation of 2-pentyne catalysed by $H_4Ru_4(CO)_{12}$ in 70 ml vials.

genation, when the carbon monoxide partial pressure is maintained lower by the use of larger vials (208 ml), all the other experimental conditions remaining unchanged.

This catalytic system is particular interesting for the initial specificity observed in the hydrogenation of 1-pentyne and 2-pentyne to 1-pentene and 2-*cis*-pentene respectively, since it can potentially be improved by using higher hydrogen pressures, as reported previously for carbonylhydrido(tributilphosphine)cobalt(I) complexes [9], in order to enhance the rate of hydrogenation compared to the rate of pentene isomerisation.

Experimental

Tetrahydridododecacarbonyltetraruthenium was prepared according to the literature [10]. 1-pentyne (Fluka, pure grade) was used without further purification, 2-pentyne (Merck, pure grade) was redistilled prior to use. Toluene, analytical reagent, was stored on molecular sieves.

Experimental apparatus and techniques, and gas chromatographic analyses of pentynes, pentenes and pentane were performed as previously described [2].

The formation of substituted derivatives of $H_4Ru_4(CO)_{12}$ was followed by tlc (absorbent Kieselgel $PF_{254+368}$ Merck, eluent petroleum ether, b.p. 40–70 °C, and 5% diethyl ether), and the disappearance of $H_4Ru_4(CO)_{12}$ was checked by i.r. spectroscopy.

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