Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Styrene and ethylene complexes of ruthenium as active intermediates in catalytic hydrogenation of olefins

SANSHIRO KOMIYA, AKIO YAMAMOTO and SAKUJI IKEDA
Research Laboratory of Resources Utilization, Tokyo Institute of Technology Ookayama, Meguro, Tokyo (Japan)

(Received June 26th, 1972)

Hydrido- and olefin-coordinated complexes of transition metals are generally regarded as the active intermediates in the catalytic hydrogenation of olefins[1], but in few cases have both types of complex been isolated from a catalytic system. We have found that dihydridotetrakis(triphenylphosphine)ruthenium(II), $RuH_2(PPh_3)_4$ (I)[2-5], an active catalyst for the hydrogenation of styrene and ethylene, yields zerovalent complexes coordinated with styrene and ethylene according to the following equations:

$$\underset{\text{(I)}}{RuH_2(PPh_3)_4} + CH_2{=}CHC_6H_5 \rightarrow \underset{\text{(II)}}{Ru(CH_2{=}CHC_6H_5)(PPh_3)_3} + PPh_3 + C_2H_5C_6H_5$$

$$\underset{\text{(I)}}{RuH_2(PPh_3)_4} + CH_2{=}CH_2 \rightarrow \underset{\text{(III)}}{Ru(C_2H_4)(PPh_3)_3} + PPh_3 + C_2H_6$$

The styrene-coordinated complex (II) was obtained as purple crystals (nc) on reaction of (I) with styrene at room temperature. Analysis found: C, 76.0; H, 5.4. $C_{62}H_{53}P_3Ru$ calcd.: C, 75.1; H, 5.4. The reaction was accompanied by the formation of 1 mole of ethylbenzene per mole of (I) as identified by gas chromatography and NMR spectroscopy. The NMR spectrum of the styrene solution containing (I) showed the peaks of ethylbenzene and two other broad peaks at τ 5.79 and 7.51 in a ratio of 1/2. These broad peaks were assigned to the vinyl protons of the styrene coordinated with ruthenium in a 1/1 ratio by comparison of the peak area with that of ethylbenzene which was formed in an equimolar quantity with (I). Since the IR spectrum of (II) shows no absorption band in the metal–hydride stretching region, and the iodolysis of (II) released no gas, the complex (II) is considered to be a zerovalent complex without a hydride ligand.

The styrene complex (II) is very unstable toward many solvents. Addition of a large excess of toluene caused the separation of a yellow precipitate which was identified as (I) on the basis of its IR spectrum which had a ν(Ru–H) band at 2080 cm^{-1} [1] and of its elemental analysis. In the decomposition of (II) in toluene to yield (I), ethylbenzene and styrene were found in a molar ratio of ca. 3/1. The combined amount of ethylbenzene and styrene was equimolar with that of (II). When tetrachloroethylene, which contains no hydrogen, was used as the solvent, the ratio of ethylbenzene to styrene sharply decreased to 1/9, indicating that the solvent is the major source of hydrogen in the decomposition of the styrene complex (II) by toluene. The formation of a small amount of ethylbenzene in the decomposition of (II) in tetrachloroethylene shows that abstraction of hydrogen from triphenylphosphine can also occur. The product from the reaction of (II) in tetrachloroethylene had the composition $Ru(C_2Cl_4)(PPh_3)_3$.

The ethylene-coordinated complex $Ru(C_2H_4)(PPh_3)_3$ (III) (nc) was prepared by the reaction of (I) in benzene with ethylene at room temperature which was accompanied by the formation of one mole of ethane per mole of (I). Analysis found: C, 73.8; H, 5.5. $C_{56}H_{49}P_3Ru$ calcd.: C, 73.4; H, 5.4. The ethylene complex (III) is white when pure, but dissolves to give a solution with a red brown colour. The IR spectrum of (III) shows no hydride absorption band.

Iodolysis of the ethylene complex (III) in benzene releases only ethylene (103% of the calculated value for $Ru(C_2H_4)(PPh_3)_3$). On the other hand, thermolysis and acidolysis of (III) gave ethane in addition to ethylene. These results suggest the possible formation of an ethylruthenium species by involvement of the *ortho* hydrogens of the triphenylphosphine ligands. Incorporation of the *ortho* hydrogens[6-9] was demonstrated in an exchange reaction of $Ru(C_2H_4)(PPh_3)_3$ in benzene with C_2D_4, which gave $C_2H_nD_{4-n}$ ($n = 0,1,2,3,4$) as revealed by mass spectroscopy. NMR and IR spectra of the triphenylphosphine oxide obtained by the oxidation of the resulting complex showed considerable deuterium exchange at the *ortho* positions of the triphenylphosphine [2].

In the catalytic hydrogenation process of styrene the colour of the solution containing the ruthenium complex depends on the relative amounts of hydrogen and styrene present in the system, and varies between yellow and purple as either the hydride or styrene-coordinated species predominates in the catalyst solution. The kinetics of the catalytic hydrogenation will be reported separately.

REFERENCES

1 J.A. Osborn, F.H. Jardine, J.F. Young and G. Wilkinson, *J. Chem. Soc. A*, (1966) 1712.
2 T. Ito, S. Kitazume, A. Yamamoto and S. Ikeda, *J. Amer. Chem. Soc.*, 92 (1971) 3011.
3 J.J. Levison and S.D. Robinson, *J. Chem. Soc. A*, (1970) 2947.
4 W.H. Knoth, *J. Amer. Chem. Soc.*, 90 (1968) 7172.
5 W.H. Knoth, *J. Amer. Chem. Soc.*, 94 (1972) 104.
6 G.W. Parshall, *Accounts Chem. Res.*, 3 (1970) 139.
7 R.A. Schunn, *Inorg. Chem.*, 9 (1970) 2567.
8 G.W. Parshall, *J. Amer. Chem. Soc.*, 90 (1968) 1669.
9 G.W. Parshall, W.H. Knoth and R.A. Schunn, *J. Amer. Chem. Soc.*, 91 (1969) 4990.