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HYDROGENATION OF OLEFINS BY μ-DICHLORO-π-BENZENE-RUTHENIUM(II)

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Some rhodium complexes bearing an aromatic π-ligand have been reported to act as effective catalysts for the hydrogenation of olefins in dimethylformamide (DMF) solution[1]. We studied the catalytic activity of μ-dichloro-π-benzene-ruthenium(II), $[Ru(C_6H_6)Cl_2]_n$ (complex 1), which also has an aromatic π-ligand, and found, to our great interest, that it shows catalytic behavior quite similar to that of the famous hydrogenation catalyst, dichlorotris(triphenylphosphine)-ruthenium(II) (complex 2), bearing three triphenylphosphine ligands instead of π-benzene ligand of complex 1.

Complex 1 used in the present experiments was prepared from $RuCl_3 \cdot 3H_2O$ and 1,3- or 1,4-cyclohexadiene by the method suggested by Winkhaus et al.[2] Hydrogenation was carried out in a glass tube inserted in a 25 ml stainless steel autoclave under 20 kg/cm^2 of hydrogen pressure at $30 \pm 0.1^\circ$ for 4 hours with constant agitation by a TEFLON-coated magnetic rotor. The reaction products were analyzed by g.l.c.[*1]

The results are summarized in Table 1. Since complex 1 is soluble in dimethyl sulfoxide (DMSO), partially soluble in DMF and substantially insoluble in usual organic solvents, the reaction proceeded almost heterogeneously in all cases except in DMSO or DMF. The catalytic activity and the ratio of the reaction products depended upon the kind of solvents and additives employed. In benzene, complex 1 had rather low catalytic activity; however, the addition of a small amount of organic base such as pyrrolidine extremely increased hydrogenation rate. The addition of a large excess of base, however, lowered the activity. To some extent, isomerization of pentene-1 to pentene-2 took place simultaneously with hydrogenation. In strongly coordinating

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[*1] Column: glutaronitrile/Diasolid L & acetonylacetone/Celite 545, each 4 mmϕ x 3 m. Temp.: r.t. Carrier gas: He.

Table 1. Results of Hydrogenation

Olefin (0.5 ml)	Solvent (3 ml)	Additive (ml)		Products Composition (%)			
				Pentane	Pentene-1	Pentene-2 (trans)	Pentene-2 (cis)
Pentene-1	Benzene	—		5	91	—	4
			0.007	91	—	7	2
		"	1.0	1	99	—	—
		Et_3N	0.01	22	46	20	12
		"	1.0	2	98	—	—
	CH_3CN	—		1	99	—	—
	DMSO	—		1	99	—	—
	DMF	—		14	1	71	14
Pentene-2*	Benzene		0.007	47	—	42	11

* trans 54%, cis 46%.

$[RuCl_2(C_6H_6)]_n$, 10 mg; H_2, 20 kg/cm^2; Temp., 30 ± 0.1°; Reaction time, 4 hr.

solvents such as acetonitrile and DMSO, the reaction scarcely proceeded. Complex 1 showed a peculiar reactivity in DMF, which is also a strongly coordinating solvent; namely, the hydrogenation and isomerization products obtained were 14% and 85%, respectively. Although the rate of hydrogenation of pentene-2 was slower than that of pentene-1, complex 1 also hydrogenated pentene-2 unlike complex 2 which is reported to hydrogenate α-olefins almost selectively[3]. This is probably due to the smaller steric hindrance in the former.

Because the results mentioned above are similar to results obtained in the case of complex 2, it would be reasonable to consider the reaction scheme to be similar, i.e., as shown in Fig. 1.

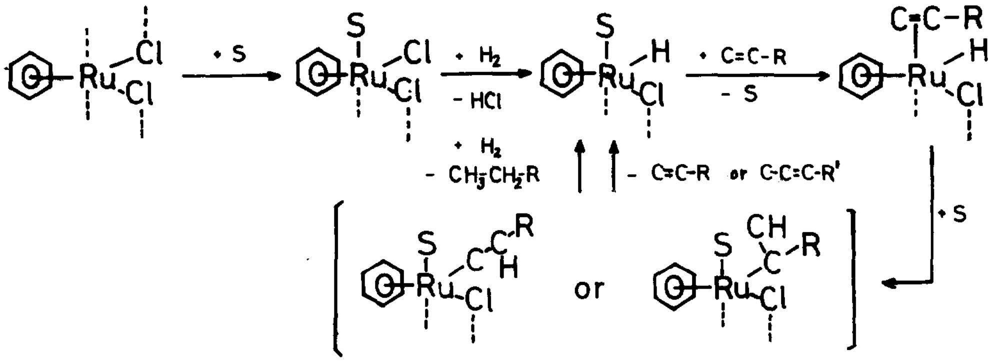

Fig. 1. A Possible Reaction Scheme

According to this scheme, it can be explained that the increase of hydrogenation activity by the addition of base arises from the fact that the base acts as an acceptor of hydrogen chloride and promotes the heterolytic splitting of hydrogen to give a hydride complex. In acetonitrile and DMSO their coordination is so strong that their displacement by olefin and thereby to be coordinatively activated would be hindered strongly. On the contrary, in DMF, the coordinative activation of molecular hydrogen in the last step of hydrogenation will be hindered by DMF. The following fact is presented in support of the formation of the complex strongly coordinated by solvent: the complex bearing DMSO (complex 3) was actually isolated as an orange powder from the solution after reaction in DMSO by high vacuum evaporation of the solvent. Further, the formation of its hydride complex was found by NMR (Fig. 2).

Complex 3 was also obtained by dissolving complex 1 in DMSO under nitrogen without olefin and hydrogen. Recrystallization from water-ethanol gave red needles, d.p. above 180°. This complex is rather stable in air; soluble in water, DMSO, acetic acid and phenol; rather sparingly soluble in chloroform, methylene dichloride and methanol; and almost completely insoluble in

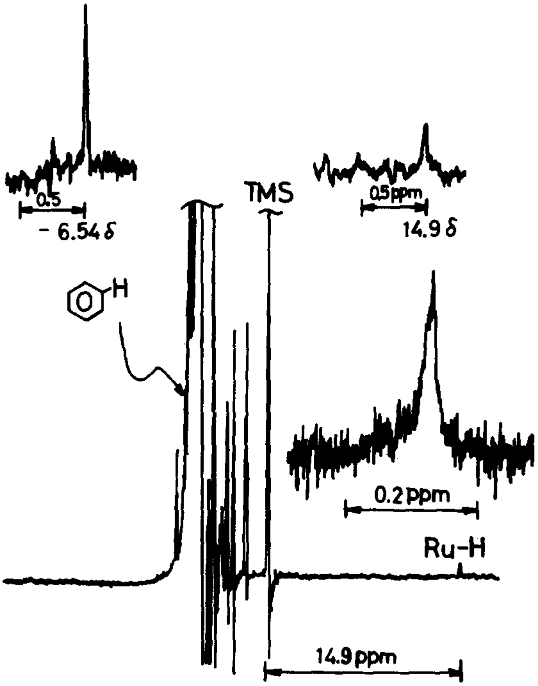

Fig. 2. NMR-spectrum of aqueous solution of complex 3 after standing with equivalent Et_3N for 4 days at r.t. under 10 kg/cm^2 of H_2.

ethanol, benzene and other usual organic solvents. Elementary analyses and IR- and NMR-spectra suggest the formula $Ru(C_6H_6)Cl_2 \cdot DMSO$[*2] which is possibly a dimer. Preliminary experiment revealed that complex 3 hydrogenates maleic acid to succinic acid in aqueous solution at room temperature under 20 kg/cm^2 of hydrogen pressure.

On allowing an aqueous solution of complex 3 and an equivalent of triethylamine to stand for 4 days at room temperature under 10 kg/cm^2 of hydrogen pressure, the light orange solution turned red-violet. In the NMR-spectrum of this solution a distinct singlet assignable to a transition metal hydride was detected at about 14.9 ppm (uncor.) upper field side from TMS[*3]. The ratio of benzene proton to metal hydride proton, 6:1 (measured in D_2O), tentatively suggests the formula $[RuClH(C_6H_6) \cdot DMSO]_2$. This may be the first example of the transition metal hydride which has a benzene ring as a ligand and, moreover, is soluble in water.

Futher studies on the catalytic reaction using this water soluble complex 3 and on complexes bearing other π-aromatic ligands are now in progress.

Acknowledgement

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References

1. V. A. Avilov, O. N. Eremenko and M. L. Khidekel, Izv. Akad. Nauk. SSSR, Ser. Khim., 1967 (12) 2781.
2. G. Winkhaus and H. Singer, J. Organometal. Chem., 7, 487 (1967).
3. P. S. Hallman, B. R. McGarvey and G. Wilkinson, J. Chem. Soc. (A), 1968, 3143.

[*2] Elementary analyses:

Found: C, 29.19; H, 3.93; Ru, 34 (by emission flame spectrometry). Calcd. for $C_8H_{12}SOCl_2Ru$: C, 29.27; H, 3.66; Ru, 30.8%.

IR-spectra measured by Shimazu IR-27G:

ν_{SO} of complex 3 (KBr disk), 1100, 1025; ν_{SO} of free DMSO (liquid film), 1055 cm^{-1}.

NMR-spectrum measured by JNM C-60HL (60MHz) in D_2O at 25° using TMS as external standard:

$C\underline{H}_3$, δ -3.22; $C_6\underline{H}_6$, δ -6.45. The ratio of peak area of methyl protons of DMSO to that of benzene protons was 1:1.

[*3] Measured in H_2O at 25° using TMS as external standard.