Journal of Organometallic Chemistry, 150 (1978) 273—278

CLUSTER RUTHENIUM HYDROGENATION CATALYSTS

PIERO FREDIANI, UGO MATTEOLI,
C.N.R., Centro di Studio sulle Cause di Deperimento e Metodi di Conservazione delle Opere d'Arte, Via Gino Capponi 9, 50121 Firenze (Italy)

MARIO BIANCHI, FRANCO PIACENTI and GLORIA MENCHI
Cattedra di Chimica Organica Industriale dell'Università di Firenze, Via Gino Capponi 9, 50121 Firenze (Italy)

(Received November 14th, 1977)

Summary

Tetraruthenium dodecacarbonyl tetrahydride and some of its phosphine-substituted derivatives have been tested as homogeneous hydrogenation catalysts. The hydrogenation of cyclohexanone in the presence of $H_4Ru_4(CO)_{12}$ is first order with respect to the catalyst concentration, the substrate concentration and the partial pressure of hydrogen. The ruthenium cluster is recovered unchanged at the end of the reaction.

Soluble hydrogenation catalysts are of potential considerable interest, since by introduction of appropriate ligands into their molecules it is possible to modify their catalytic characteristics. Several reductions of aldehydes and ketones by the use of soluble cobalt [1—7], rhodium [1,8—16], iridium [1,15,17], and ruthenium [18—20] catalysts have been reported in the literature. The complexes used were generally mononuclear or such as to give under the reaction conditions active complexes which the authors thought to be mononuclear [8].

In order to get informations on the hydrogenation of organic substrates by metal cluster catalysts we have carried out a kinetic investigation on the hydrogenation of cyclohexanone catalyzed by $H_4Ru_4(CO)_{12}$. Complexes deriving by partial replacement of carbonyl ligands in $H_4Ru_4(CO)_{12}$ by PPh_3, PBu_3 and (—)-DIOP have also been tested as catalysts for this reaction.

Results

(1) Kinetics of the hydrogenation of cyclohexanone in the presence of $H_4Ru_4(CO)_{12}$

Cyclohexanone was chosen as substrate for the kinetic investigation of the

TABLE 1

HYDROGENATION OF CYCLOHEXANONE IN THE PRESENCE OF $H_4Ru_4(CO)_{12}$: THE INFLUENCE OF SOLVENT ON THE RATE

(Cyclohexanone 9.76 g; solvent 30 ml; $H_4Ru_4(CO)_{12}$ 0.05 g; $p(H_2)$ 100 atm; T 100°C)

Solvent	Products	% Conversion after		
		30 min	60 min	90 min
n-Hexane	Cyclohexanol	trace	1.0	1.8
Cyclohexane	Cyclohexanol	trace	trace	1.8 [a]
Benzene	Cyclohexanol	trace	trace	0.9
Methanol	Cyclohexanol	11.7	25.4	36.5
	1,1-Dimethoxycyclohexane	15.5	12.8	11.3
	Cyclohexenyl methyl ether	4.6	5.0	3.6
	Cyclohexyl methyl ether	3.7	7.1	8.9
n-Propanol	Cyclohexanol	13.0	38.8	56.0
	1,1-Dipropoxycyclohexane	4.2	3.5	2.2
	Cyclohexenyl propyl ether	1.9	1.4	1.0
	Cyclohexyl propyl ether	3.3	9.3	10.0
Isopropanol	Cyclohexanol	29.6	58.4	75.1
	Cyclohexyl isopropyl ether	1.5	2.8	3.5
t-Butanol	Cyclohexanol	30.4	66.4	86.6
Diethyl ether	Cyclohexanol	2.0	4.9	8.1
Tetrahydrofuran	Cyclohexanol	34.0	59.6	75.0
Dioxane	Cyclohexanol	1.3	3.8	5.5
Pyridine	Cyclohexanol	0.7	2.8	4.7
Cyclohexane + pyridine [b]	Cyclohexanol	0.9	2.1	3.5

[a] Reaction time 120 min. [b] Pyridine 0.1 ml in cyclohexane 30 ml.

hydrogenation catalytic activity of $H_4Ru_4(CO)_{12}$ because only one product, cyclohexanol is formed in tetrahydrofuran. Under fairly mild conditions, 100°C and 100 atm $p(H_2)$, in this solvent the reaction rate is appropriate for a kinetic investigation. The choice of tetrahydrofuran was made after experiments carried out in various solvents which gave the results summarized in Table 1.

The data show that high hydrogenation rates accompanied by lower selectivities are obtained in alcohols. With methyl alcohol as solvent, cyclohexyl methyl ether is the only product, other than cyclohexanol, present at the end of the reaction. This mixed ether is formed by the following series of reactions, as shown by the change with time of the concentration of the intermediates shown

SCHEME 1

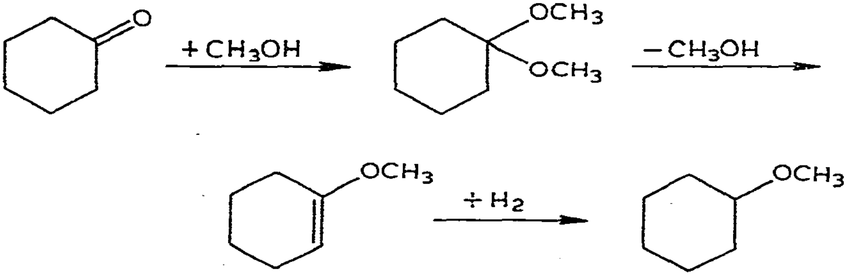

TABLE 2

HYDROGENATION OF CYCLOHEXANONE IN THE PRESENCE OF $H_4Ru_4(CO)_{12}$

(Cyclohexanone 9.76 g; THF 30 ml; $H_4Ru_4(CO)_{12}$ 0.05 g; $p(H_2)$ 100 atm; T 100°C)

Reaction time (min)	Conversion (%)	$K \times 10^2$ (min^{-1})
15	21.6	1.62
31	34.4	1.36
45	48.5	1.47
60	59.6	1.51
75	67.7	1.50

TABLE 3

HYDROGENATION OF CYCLOHEXANONE IN THE PRESENCE OF $H_4Ru_4(CO)_{12}$, AND THE INFLUENCE OF THE CATALYST CONCENTRATION ON THE RATE

(Cyclohexanone 9.76 g; THF 30 ml; $p(H_2)$ 100 atm; reaction time 31 min; T 100°C)

Catalyst concentration ($mol\ l^{-1}$)	Conversion (%)	K_2 ($l\ mol^{-1}\ min^{-1}$)
0.348	8.2	7.90
0.667	15.4	8.08
0.835	17.6	7.47
1.668	34.4	8.12
2.502	44.0	7.47
3.339	53.9	7.47
4.177	62.7	7.61

TABLE 4

HYDROGENATION OF CYCLOHEXANONE IN THE PRESENCE OF $H_4Ru_4(CO)_{12}$ AND THE INFLUENCE OF THE HYDROGEN PRESSURE ON THE RATE

(Cyclohexanone 9.76 g; THF 30 ml; $H_4Ru_4(CO)_{12}$ 0.05 g; reaction time 31 min; T 100°C)

$p(H_2)$ (atm)	Conversion (%)	$K_1 \times 10^4$ ($min^{-1}\ atm^{-1}$)
70	24.7	1.30
94	32.3	1.34
100	34.4	1.36
117	35.5	1.21
119	36.7	1.24
136	40.5	1.23
174	46.1	1.14
266	58.0	1.05

in Scheme 1. The corresponding mixed ethers are obtained when other primary or secondary alcohols are used as solvent. In hydrocarbons and dioxane very good selectivity was combined with a very low reaction rate.

After the hydrogenation of cyclohexanone in tetrahydrofuran the catalyst could be recovered unchanged. The reaction order with respect to the concentration of the organic substrate was determined from a series of reactions which were interrupted at varying degrees of conversion by rapid cooling. The reaction

TABLE 5

HYDROGENATION OF CYCLOHEXANONE IN THE PRESENCE OF $H_4Ru_4(CO)_xL_y$ COMPLEXES

(Cyclohexanone 9.76 g; THF 30 ml; Catalyst 0.067 mmol; $p(H_2)$ 100 atm; T 100°C)

Catalyst	% Conversion after		
	6 h	12 h	24 h
$H_4Ru_4(CO)_{10}(PPh_3)_2$	8.6	20.7	34.8
$H_4Ru_4(CO)_9(PPh_3)_3$	13.5	29.1	42.8
$H_4Ru_4(CO)_8(PPh_3)_4$	54.3	65.6	79.7
$H_4Ru_4(CO)_9(PBu_3)_3$	4.5	6.6	7.6
$H_4Ru_4(CO)_8(PBu_3)_4$	16.0	n.d.	49.4
$H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$	7.0	12.5	31.9

was assumed to have started at the moment of breaking the glass tube which contained the catalyst. The pressure was kept constant throughout the reaction by supplying hydrogen from a high pressure reservoir. The results are shown in Table 2.

The order with respect to the concentration of the catalyst and to the partial pressure of hydrogen was determined by carrying out two series of experiments (interrupted after 31 minutes) in which, while keeping all the other reaction parameters constant, the one under investigation was varied over a suitable range. The results of these last two series of tests are reported in Tables 3 and 4.

Hexadeuteroacetone was also hydrogenated under the conditions used for the kinetics experiments, and gave only propan-2-ol-1,1,1,3,3,3-d_6.

(2) Hydrogenation of cyclohexanone in the presence of phosphine derivatives of $H_4Ru_4(CO)_{12}$

The complexes tested as catalysts in the hydrogenation of cyclohexanone were $H_4Ru_4(CO)_{10}(PPh_3)_2$, $H_4Ru_4(CO)_9(PPh_3)_3$, $H_4Ru_4(CO)_8(PPh_3)_4$, $H_4Ru_4(CO)_9(PBu_3)_3$, $H_4Ru_4(CO)_8(PBu_3)_4$, and $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$. Experimental conditions including the molar concentration of the catalysts were the same throughout.

The reaction course was followed by removal of small portions of the reaction medium at desired intervals of time followed by GLC analysis. The results obtained are shown in Table 5.

Discussion

The rate of hydrogenation of cyclohexanone to cyclohexanol under the conditions used is directly proportional to the concentration of the substrate and to the partial pressure of hydrogen. This result is analogous to those reported in the literature for the hydrogenation of organic substrates using both mononuclear and polynuclear transition metal complexes.

The rate is also directly proportional to the concentration of the catalyst. This differs from the behaviour reported by Markò et al. [8] for the hydrogenation of aldehydes in the presence of $Rh_4(CO)_{12}$, since in that case the rate was proportional to 1/6 of the concentration of the catalyst: a mononuclear rhodium complex was thought to be the real catalyst.

The recovery at the end of our reactions, of the unchanged catalyst suggests that it retains the initial arrangement of the metal atoms in the molecule throughout the reaction. The considerable differences in rates between various solvents suggest that the solvent assists the reaction, probably by involvement in the catalytically active intermediate.

The partial replacement of the carbonyl groups in $H_4Ru_4(CO)_{12}$ by phosphine, led in all cases to a decrease of the hydrogenating activity. However, progressive replacement of the carbonyl ligands of $H_4Ru_4(CO)_{12}$ by phosphines causes an increase in activity. In the case of the tetrasubstituted complexes, the activity decreases on going from PPh_3 to PBu_3 to DIOP derivatives. The increase in the activity of the carbonylruthenium hydrides with increasing phosphine substitution is analogous to the behaviour of the phosphine-substituted mononuclear carbonylcobalt hydrides [2]. Tetracarbonylcobalt hydride, however, has an activity much lower than that of its phosphine-substituted derivatives, while $H_4Ru_4(CO)_{12}$ is more active than its phosphine-substituted derivatives.

The sole formation of $CD_3CHOHCD_3$ on hydrogenation of hexadeuteroacetone proves that this ketone is not present, at least during the reduction step, in its enol form. It must interact with the catalyst through its carbonyl group, probably by a mechanism analogous to that suggested for the hydrogenation of aldehydes and ketones by carbonyl-cobalt [1] and -rhodium hydrides [8].

Experimental

Materials

Cyclohexanone, C. Erba product, was purified by distillation.

Tetrahydrofuran, C. Erba product, was refluxed over sodium then over $LiAlH_4$ and rectified under nitrogen.

Hexadeuteroacetone, Sorin product, 99.8% isotopic purity.

Catalysts

$H_4Ru_4(CO)_{12}$; $H_4Ru_4(CO)_{10}(PPh_3)_2$; $H_4Ru_4(CO)_{12-y}L_y$ ($L = PPh_3, PBu_3$; $y = 3,4$); and $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ were prepared as previously described [21,22].

Hydrogenation experiments

The catalyst, placed in a sealed glass tube under nitrogen, was introduced into a 125 ml rocking autoclave on an appropriate support in order to avoid the contact between catalyst and substrate. Air was removed, a solution of cyclohexanone in tetrahydrofuran was introduced under nitrogen, and finally hydrogen was added to the appropriate pressure. The autoclave was then heated to 100°C. After one hour, when the system had reached thermal equilibrium, the tube containing the catalyst was broken and reaction commenced. Hydrogen was continuously supplied from a high pressure vessel to keep the pressure constant. Reactions were quenched at the desired times by rapid cooling with water, and the products immediately analyzed by GLC (Perkin—Elmer F30 intrument equipped with 2 m columns containing Ucon oil LB 550 X on Chromosorb W 15/85). Identification of the products was through their IR and mass spectra.

Hydrogenation of CD_3COCD_3

CD_3COCD_3 (2.4 g), $H_4Ru_4(CO)_{12}$ (20 mg), hydrogen (100 atm) at 100°C have given $CD_3CHOHCD_3$ in 57% yield whose NMR spectrum showed δ(int. TMS, $CDCl_3$): 2.5 (s, 1.0 H, CHO$\underline{H}$); 4.95 (s, 1.0 H, $\underline{CH}$OH).

Acknowledgements

We thank Dr. Gloriano Moneti, Facoltà di Farmacia, University of Florence for recording the mass spectra.

The research was financially supported by C.N.R., Roma.

References

1 M.E. Vol'pin and I.S. Kolomnikov, Russian Chem. Rev., 38 (1969) 273.
2 G.F. Pregaglia, A. Andreetta, G.F. Ferrari and R. Ugo, J. Organometal. Chem., 30 (1971) 387.
3 C. Bresson and R. Broggi, Chim. Ind. (Milan), 50 (1968) 1194.
4 L. Markò, B. Heil and S. Vastag, Advan. Chem. Ser., No. 132, Amer. Chem. Soc., Washington, D.C., 1974, p. 27.
5 Y. Ohgo, S. Takeuchi and J. Yoshimura, Bull. Chem. Soc. Japan, 44 (1971) 583.
6 Y. Ohgo, Y. Natori, S. Takeuchi and J. Yoshimura, Chem. Lett., (1974) 709.
7 R.W. Waldron and J.H. Weber, Inorg. Chim. Acta, 18 (1976) L3.
8 B. Heil and L. Markò, Acta Chim. Acad. Sci. Hung., 55 (1968) 107.
9 R.R. Schrock and J.A. Osborn, Chem. Commun., (1970) 567.
10 P. Bonvicini, A. Levi, G. Modena and G. Scorrano, Chem. Commun., (1972) 1188.
11 M. Tanaka, Y. Watanabe, T. Mitzudo, H. Iwane and Y. Takegami, Chem. Lett., (1973) 239.
12 C.J. Sih, J.B. Heather, G.P. Peruzzotti, P. Price, R. Sood and L. Lan-Fong Hsu, J. Amer. Chem. Soc., 95 (1973) 1676.
13 A. Levi, G. Modena and G. Scorrano, Chem. Commun., (1975) 6.
14 B. Heil, S. Toros, S. Vastag and L. Markò, J. Organometal. Chem., 94 (1975) C47.
15 J. Solodar, Chem. Techn., (1975) 421.
16 S. Meguro, T. Mizoroki and A. Ozaki, Chem. Lett., (1975) 943.
17 K.A. Taylor, Advan. Chem. Series, No. 70, Amer. Chem. Soc., Washington, D.C., (1968), p. 195.
18 P. Frediani, M. Bianchi and F. Piacenti, Chim. Ind. (Milan), 55 (1973) 543.
19 H. Hirai, T. Furuta and S. Makishima, Japan Pat. 71 39,326, 1971; Chem. Abstr., 76 (1972) 45743.
20 C. Botteghi, M. Bianchi, E. Benedetti and U. Matteoli, Chimia, 29 (1975) 256.
21 F. Piacenti, M. Bianchi, P. Frediani and E. Benedetti, Inorg. Chem., 10 (1971) 2759.
22 C. Botteghi, S. Gladiali, M. Bianchi, U. Matteoli, P. Frediani, P.G. Vergamini and E. Benedetti, J. Organometal. Chem., 140 (1977) 221.