Journal of Organometallic Chemistry, 275 (1984) 113–117
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

(η^6-ARENE)(η^4-CYCLOOCTA-1,5-DIENE)RUTHENIUM(0) COMPLEXES AS HOMOGENEOUS HYDROGENATION CATALYSTS

PAOLO PERTICI, GIOVANNI VITULLI, CLARA BIGELLI and RAFFAELLO LAZZARONI

Centro C.N.R. per le Macromolecole Stereoordinate ed Otticamente Attive, Istituto di Chimica Organica, Università di Pisa, 56100 Pisa (Italy)

(Received May 10th, 1984)

Summary

Ru(η^6-arene)(η^4-COD) complexes (COD = cycloocta-1,5-diene) have been found to be catalytic precursors for the homogeneous hydrogenation of α-olefins and cycloolefins under mild conditions (room temperature, $P(H_2)$ 1–20 atm).

Introduction

There is current interest in the use of arene-ruthenium compounds as hydrogenation catalysts [1]. In the presence of bases, $[RuCl_2(\eta^6\text{-arene})]_2$ complexes (arene = benzene, mesitylene, 1,3,5-triphenylbenzene) were found to be active in the hydrogenation of α-olefins under mild conditions [2,3]. More recently the catalytic hydrogenation of aromatic hydrocarbons using arene or arene-hydride ruthenium complexes has been reported [4,5]. However, only a limited number of synthetic routes to such species are available [1]. They are normally difficult to prepare and this has prevented extensive studies on their chemistry and catalytic activity. Recently we found a simple route to arene-cyclooctadiene ruthenium complexes by the reaction of arenes with Ru(η^6-COT)(η^4-COD) (COT = cycloocta-1,3,5-triene) under an atmosphere of hydrogen [6]. These complexes have been tested as hydrogenation catalyst and we report here the results obtained in the hydrogenation of olefinic compounds.

Results and discussion

Ru(η^6-arene)(η^4-COD) complexes are attractive compounds for use as homogeneous hydrogenation catalysts. Cyclooctadienes bonded to transition metals can be reduced easily under hydrogenation conditions, giving active coordinatively-unsaturated intermediates [7]. The arene–metal bond, on the other hand, can be strong enough to stabilize changes in oxidation states, stereochemistry, and coordination number during the catalytic reaction [8].

0022-328X/84/$03.00

We have investigated the hydrogenation of α-olefins and cyclo-olefins using the arene complexes as catalytic precursors, in order to evaluate their catalytic activity, especially under mild conditions, and to test the potential use of the analogous chiral complexes in asymmetric hydrogenation. The results are summarized in Table 1.

The hydrogenation of 1-pentene and 1-hexene takes place easily under mild conditions. At room temperature and at a hydrogen pressure of one atmosphere, a conversion of ca. 20% after 48 h has been obtained (runs 1,2). The reaction is considerably faster at higher pressures. At 20 atm the olefins are completely reduced to the corresponding alkanes in ca. 10 h (runs 3,4).

Vinylidenic defins and cycloolefins are reduced to the same extent as α-olefins when working at 20 atm (runs 5,6).

The hydrogenation of 1,5-COD has also been examined. The reaction is very slow

TABLE 1

HYDROGENATION OF OLEFINS IN THE PRESENCE OF Ru(η^6-ARENE)(η^4-COD) COMPLEXES IN THF (3 ml) AT ROOM TEMPERATURE

Run	Catalyst (mmol)	Substrate (mmol)	P_{H_2} [a] (atm)	Time (h)	Products (%)
1	Ru(benzene)(COD) (0.15)	1-pentene (14)	1	48	n-pentane (24)
2	Ru(benzene)(COD) (0.15)	1-hexene (12)	1	48	n-hexane (17)
3	Ru(benzene)(COD) (0.18)	1-pentene (28)	20	10	n-pentane (99)
4	Ru(benzene)(COD) (0.18)	1-hexene (25)	20	10	n-hexane (99)
5	Ru(benzene)(COD) (0.20)	2-ethyl-1-hexene (28)	20	12	3-methylheptane (99)
6	Ru(benzene)(COD) (0.24)	Cyclohexene (25)	20	12	cyclohexane (99)
7	Ru(benzene)(COD) (0.20)	1,5-COD (22)	1	24	cyclooctane (traces) cyclooctene (2) 1,3-COD(traces) 1,4-COD(traces)
8	Ru(benzene)(COD) (0.20)	1,5-COD (22)	20	12	cyclooctane (4) cyclooctene (15) 1,3-COD(2) 1,4-COD(2)
9	Ru(benzene)(COD) (0.21)	1,5-COD (22)	60	70	cyclooctane (38) cyclooctene (62)
10	Ru(benzene)(COD) (0.20)	benzene (30)	20	12	no hydrogenation
11	Ru(*p*-xylene)(COD) (0.22)	1-pentene (28)	20	12	n-pentane (99)
12	Ru(*p*-xylene)(COD) (0.22)	2-ethyl-1-hexene (28)	20	13	3-methylheptane (99)
13	Ru(mesitylene)(COD) (0.20)	1-pentene (25)	20	12	n-pentane (99)
14	Ru(mesitylene)(COD) (0.20)	2-ethyl-1-hexene (28)	20	13	3-methylheptane (99)

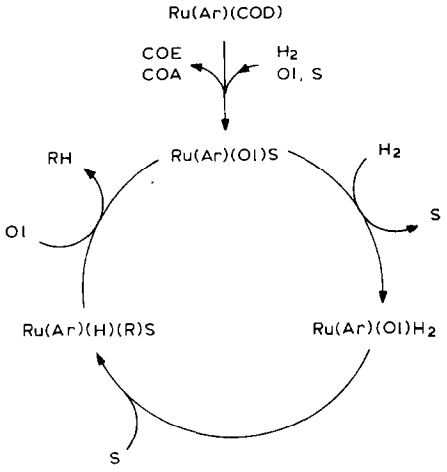
[a] Starting pressure.

at a pressure of one atmosphere (run 7) and only traces of hydrogenated products have been detected after 24 h. At 20 atm the diene gives a mixture of cyclooctene and cyclooctane with a conversion of ca. 20% (run 8), while at 60 atm (run 9) it is completely hydrogenated in 70 h to give cyclooctene (62%) and cyclooctane (38%). Small amounts of isomerization products (1,3- and 1,4-cyclooctadiene) can be detected when the reaction has not gone to completation (runs 7,8). Some selectivity towards cyclooctene can also be observed, the amount of cyclooctene being significatively higher than cyclooctane (runs 7–9).

Aromatic compounds are not hydrogenated under the reaction conditions used (run 10).

It is noteworthy that no difference has been observed using catalysts containing different arene ligands (runs 3,5,11–14). This is in contrast to the hydrogenation of olefins by $[RuCl_2(\eta^6\text{-arene})]_2$ complexes [2] and may be related to the higher stability of the arene–metal bond in the $Ru(\eta^6\text{-arene})(\eta^4\text{-COD})$ compounds, which give no arene exchange reactions even at high temperature or under UV radiation [9].

The mechanism of the hydrogenation is probably complicated. Some observations, however, can be made. The solvent seems to play an important role in the reaction. With tetrahydrofuran, the solution was completely clear during and at the end of the reaction, while with n-pentane, benzene or without solvents, some amounts of decomposition products have been observed. It seems reasonable to suppose that coordinating solvents probably stabilize a coordinatively-unsaturated arene-ruthenium compound, formed by hydrogenation of the 1,5-COD initially bonded to ruthenium. Cyclooctene and/or cyclooctane were always detected in the reaction products of the olefin hydrogenation. Coordination of the olefin substrate and oxidative addition of hydrogen can lead, in a subsequent step of the reaction, to arene-olefin hydride ruthenium compounds, which can be regarded as active hydro-



(Ol = olefin , Ar = arene , S = solvent ,
COE = cyclooctene , COA = cyclooctane)

SCHEME 1. Proposed catalytic cycle for hydrogenation. The upper part of the scheme represents catalyst activation and the lower part represents the cycle itself.

genation intermediates [5]. It is also of interest that in the hydrogenation of 1,5-COD, where no solvent effect has been observed, the starting complex Ru(η^6-arene)(η^4-COD) can be recovered quantitatively, suggesting that arene-olefin ruthenium complexes may be closely involved in the catalytic reaction. On the basis of the above discussion a hydrogenation mechanism can be tentatively suggested, as shown in Scheme 1.

The possibility of preparing chiral Ru(η^6-arene)(η^4-diene) complexes containing optically active arene ligands [10], makes this kind of compound of interest as possible new catalysts for the asymmetric hydrogenation of prochiral olefins.

Experimental

The ruthenium complexes were prepared and handled in a dry oxygen-free nitrogen atmosphere, using conventional Schlenk-tube techniques. Solvents were purified by conventional methods, and distilled and stored under nitrogen. Arene ligands (Farmitalia-Carlo Erba products) were distilled prior to use. GLC analysis of the products of the catalytic hydrogenations were carried out on a Perkin-Elmer F30 apparatus equipped with columns (length 2 m) packed with squalane, carbowax 20M or silicone on Chromosorb W80/100. ^{1}H NMR spectra of the Ru(η^6-arene)(η^4-COD) complexes were obtained in [$^2H_6$]benzene solution, using TMS as internal standard, on a Varian T-60 spectrometer.

Synthesis of Ru(η^6-COT)(η^4-COD)

This complex was synthesized by the reaction of $RuCl_3 \cdot 3H_2O$ with COD in the presence of zinc dust and ethanol [11].

Synthesis of Ru(η^6-arene)(η^4-COD) (arene = benzene, p-xylene, mesitylene)

These complexes were prepared by reaction of Ru(η^6-COT)(η^4-COD) with the corresponding arene in the presence of hydrogen, according to the general method previously reported [6]. The preparation of Ru(η^6-mesitylene)(η^4-COD) will be described in detail.

The complex Ru(η^6-COT)(η^4-COD) (150 mg, 0.47 mmol) was dissolved in mesitylene (3 ml, 22 mmol) and the solution was shaken at room temperature under hydrogen at atmospheric pressure for 8 h. The excess of mesitylene was removed under vacuum (0.2 mmHg) and the residue was extracted with n-pentane (50 ml). The yellow solution was concentrated to 5 ml and cooled to $-78\,^\circ$C, to give 145 mg (0.44 mmol, yield 95%) of Ru(η^6-mesitylene)(η^4-COD). The ^{1}H NMR spectrum showed resonances at δ 4.85 (s, 3H), 3.1 (m, 4H), 2.3 (m, 8H), 1.75 (s, 9H) ppm.

Catalytic hydrogenation experiments

All the hydrogenation experiments were performed in a stainless-steel autoclave (125 ml). In a typical experiment (run 4, Table 1) a glass vial, containing Ru(η^6-benzene)(η^4-COD) (50 mg, 0.18 mmol), THF (3 ml), and 1-hexene (3.1 ml, 25 mmol), was introduced into the autoclave, under nitrogen. The nitrogen was removed under vacuum and the autoclave was charged with hydrogen (20 atm).

The autoclave was stirred at room temperature until hydrogen absorption finished (10 h). The autoclave was discharged and the yellow solution was distilled under vacuum (1 mmHg). The distillate was collected in a trap cooled to $-196\,^\circ$C and

analyzed using GLC. It contained n-hexane (99%) and a mixture of hexenes (traces), as well as THF. The yellow solid residue was the starting complex (43 mg, 0.15 mmol; ^{1}H NMR: δ (ppm) 4.95 (s, 6H), 3.6 (m, 4H), 2.4 (m, 8H)).

References

1 R.G. Gastinger and K.J. Klabunde, Transition Met. Chem., 4 (1979) 1.
2 R. Iwata and I. Ogata, Tetrahedron, 29 (1973) 2753.
3 A.G. Hinze, Recl. Trav. Chim. Pays-Bas, 92 (1973) 542.
4 J.W. Johnson and E.L. Muetterties, J. Am. Chem. Soc., 99 (1977) 7395.
5 M.A. Bennett, T.M. Huang, A.K. Smith and T.W. Turney, J. Chem. Soc., Chem. Commun., (1978) 582; M.A. Bennett, T.M. Huang, T.W. Turney, ibid., (1979) 312; H. Werner and R. Werner, J. Organomet. Chem., 174 (1979).
6 P. Pertici, G. Vitulli, R. Lazzaroni, P. Salvadori and P.L. Barili, J. Chem. Soc., Dalton Trans., (1982) 1019.
7 R.R. Schrock and J.A. Osborn, J. Am. Chem. Soc., 98 (1976) 2134.
8 P.M. Maitlis, Chem. Soc. Rev., 10 (1981) 1.
9 E.L. Muetterties, J.R. Bleeke and A.C. Sievert, J. Organomet. Chem., 178 (1979) 197.
10 P. Pertici, G. Vitulli, C. Bigelli, P.L. Barili and R. Lazzaroni, XV Congresso Nazionale Chimica Inorganica, A.I.C.I. and S.C.I., Bari (Italy), 1983, A2.
11 P. Pertici, G. Vitulli, M. Paci and L. Porri, J. Chem. Soc., Dalton Trans., (1980) 1961.