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SELECTIVE HYDROFORMYLATION OF CYCLODIENES TO CYCLOALKENECARBOXALDEHYDES USING CATALYSTS DERIVED DIRECTLY FROM Rh VAPOUR AND CYCLODIENES

PIERO SALVADORI, GIOVANNI VITULLI, ANDREA RAFFAELLI and RAFFAELLO LAZZARONI

Centro di Studio del C.N.R. per le Macromolecole Stereoordinate ed Otticamente Attive c/o Istituto di Chimica Organica, Università di Pisa, Via Risorgimento, 35 56100 Pisa (Italy)

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Summary

Cocondensation of Rh atoms with cyclodienes at liquid nitrogen temperature yields Rh complexes, thermally stable in excess of the ligand, which are good catalysts for the selective hydroformylation of cyclodienes to cycloalkenecarboxaldehydes.

Introduction

Since its development the metal atom technique has been widely employed in organometallic chemistry [1]. However, although it provides a rapid and convenient method of obtaining new potentially catalytic systems, it has until recently found little application in catalysis [2].

In catalytic systems directly prepared by reaction of metal vapour and organic substrates like alkenes, alkynes, arenes, the metal is expected to be in a low oxidation state and the complex obtained weakly stabilized by the ligand. Such compounds therefore should have a catalytic ability to rival that of the best known catalysts. Toluene-solvated rhodium atoms, for instance, have been recently found to be very active in the catalytic hydrogenation of olefinic and aromatic compounds at room temperature and atmospheric pressure [3]. We now report that cyclodienes can be selectively hydroformylated to cycloalkenecarboxaldehydes, using the cocondensation products of Rh vapour and cyclodiolefins as catalytic precursors.

The hydroformylation of cyclodienes has been previously reported using conventional Rh compounds as catalytic precursors, but no appreciable selectivity in cycloalkenecarboxaldehydes was found [4].

Results and discussion

The cocondensation of Rh vapour with a large excess of cyclodienes at liquid nitrogen temperature affords, on warming up, red-brown solutions which have been

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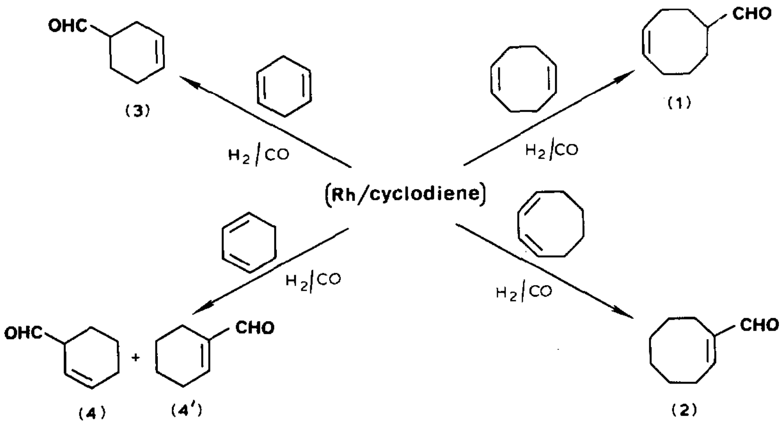
directly used in the hydroformylation of cyclodienes. Cycloocta-1,5-diene (1,5-COD), cycloocta-1,3-diene (1,3-COD), cyclohexa-1,4-diene (1,4-CHD) and cyclohexa-1,3-diene (1,3-CHD) have been used as cyclodiolefinic substrate.



SCHEME 1

The hydroformylation takes place at low temperature (20–50°C) under a CO/H_2 (1/1) pressure of 70 atm, giving cycloalkenecarboxaldehydes as the selectively only products (Scheme 1). The hydroformylation of cyclodiolefins with isolated double bonds, such as 1,5-COD and 1,4-CHD, produces the corresponding cycloalkenecarboxaldehyde, cyclooct-4-enecarboxaldehyde (**1**) and cyclohex-3-enecarboxaldehyde (**3**), respectively. In the hydroformylation of 1,3-COD only the conjugated isomer, cyclooct-1-enecarboxaldehyde (**2**) is formed. On the other hand the hydroformylation of 1,3-CHD gives two products, cyclohex-2-enecarboxaldehyde (**4**) and cyclohex-1-enecarboxaldehyde (**4′**) in about 90 and 10% yields, respectively. Since the isomerization of cyclohex-2-enecarboxaldehyde to cyclohex-1-enecarboxaldehyde (**4** → **4′**) has been found to occur very easily under the working conditions, it can reasonably be assumed that in the case of 1,3-COD also the first hydroformylation product is the cyclooct-2-enecarboxaldehyde, which readily isomerizes to the conjugated isomer, **2**.

The products were isolated and characterized by mass and ^1H NMR spectra. The ^1H NMR spectra of the compounds **1**, **3** and **4** show a doublet at δ 9.72, 9.85 and 9.72 ppm, respectively, attributable to the aldehydic proton coupled with the α ring proton, and a multiplet around 5.5–6.1 ppm due to the two olefinic protons. The ^1H NMR spectra of the compounds **2** and **4′** are characteristic of α-β unsaturated cyclic aldehydes, showing a singlet for the aldehydic proton at δ 9.58 and 9.52 ppm, respectively, and a triplet for the olefinic proton at 6.82 and 6.85 ppm, respectively. No traces of dialdehydes or saturated monoaldehydes have been detected. All runs gave reproducible results which have been summarized in Table 1.

The catalytic activity under mild conditions and the selective formation of cycloalkenecarboxaldehydes are the main features of the catalytic systems prepared from Rh vapour and cyclodienes. The hydroformylation of the above cyclodienes using traditional Rh catalysts has generally been carried out at temperatures and pressures higher than those required for catalytic systems made from Rh vapour.

TABLE 1

HYDROFORMYLATION OF CYCLODIOLEFIN SUBSTRATES BY THE PRODUCTS OF COCONDENSATION OF Rh ATOMS WITH DIENES [a]

Substrate	Substrate/Rh (mol/g.atom)	Temperature (°C)	Conversion (%)	Products [b]	
1,5-COD	200	20	80	4-COE (1)	
1,3-COD	200	20	25	1-COE (2)	
1,4-CHD	270	50	50	3-CEE (3)	
1,3-CHD	270	50	40	2-CEE (4)	90%
				1-CEE (4')	10%

[a] Reaction time, 48 h; initial pressure CO/H_2 (1/1), 70 atm. [b] 4-COE = cyclooct-4-enecarboxaldehyde; 1-COE = cyclooct-1-enecarboxaldehyde; 3-CEE = cyclohex-3-enecarboxaldehyde; 2-CEE = cyclohex-2-enecarboxaldehyde; 1-CEE = cyclohex-1-enecarboxaldehyde.

Using $Rh(CO_2CH_3)(CO)(PPh_3)_2$ as catalyst, the hydroformylation of cyclic C_6 dienes with CO/H_2 (1/1) in benzene at 100°C and 100 atm gave mainly dialdehydes in yields of about 70%, whereas cyclic C_8 dienes gave similar yields of saturated monoaldehyde under the same conditions. Under milder conditions (60°C and 60 atm) only 1,5-COD reacts, giving the unsaturated monoaldehyde as a mixture of two isomers [4]. In order to provide a direct comparison between the catalysts prepared via the metal atom method and the conventional ones, we studied the hydroformylation of 1,5-COD, one of the most investigated cyclodienes, using traditional Rh catalysts at room temperature and $P(H_2/CO)$ (1/1) of 70 atm. The results are summarized in Table 2. While the reaction does not take place with Rh_2O_3 and $Rh_6(CO)_{16}$ under these conditions, $Rh_4(CO)_{12}$ and $HRh(CO)(PPh_3)_3$ are active. Their activity, however, is lower than that showed by the catalytic systems prepared by the metal atom method. Nevertheless the reaction shows a high selectivity, the cyclooct-4-enecarboxaldehyde beeing the only product. Therefore mild conditions are very important in obtaining a good selectivity, and catalytic systems prepared by the metal atom method seem to be the best when both activity and selectivity are taken into account.

The active hydroformylation species, which could be hydridocarbonyl Rh complexes containing a cyclodiene moiety, are probably the same as those present when starting from some traditional catalysts, as $Rh_4(CO)_{12}$, or from the Rh/cyclodiene

TABLE 2

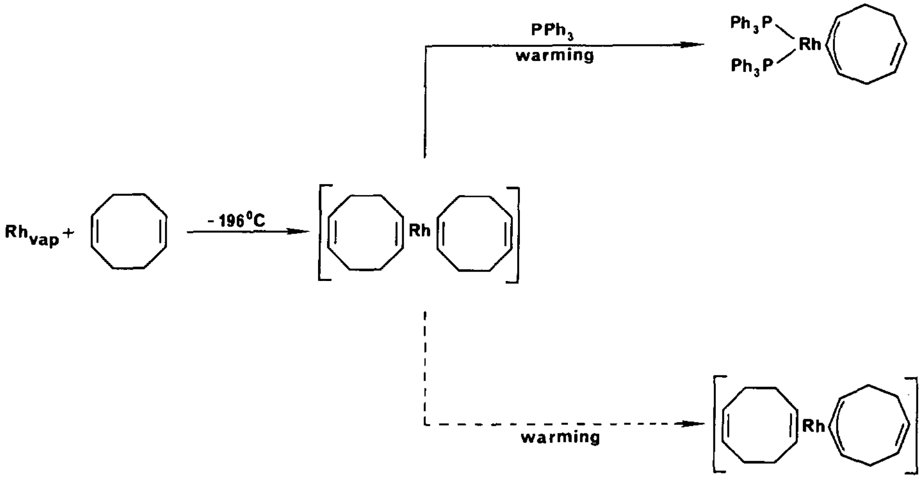
HYDROFORMYLATION OF 1,5-COD USING VARIOUS CATALYTIC PRECURSORS [a]

Catalytic precursor	Substrate/Rh (mol/g.atom)	Conversion (%)	$\overline{TN}_{48h} \times 10^{-3}$ [b] (sec^{-1})	Products [c]
Rh/1,5-COD	200	80	0.95	4-COE
Rh_2O_3	260	–	–	–
$Rh_6(CO)_{16}$	360	traces	–	–
$Rh_4(CO)_{12}$	200	25	0.28	4-COE
$HRh(CO)(PPh_3)_3$	1000	8	0.46	4-COE

[a] Reaction time, 48 h; initial pressure CO/H_2 (1/1), 70 atm; temperature, 20°C. [b] $\overline{TN}_{48h}$ = average turnover number after 48 h. [c] 4-COE = cyclooct-4-enecarboxaldehyde.

cocondensation products, but however may be formed more easily and perhaps in higher concentration from these latter complexes.

In order to elucidate the nature of the catalytic precursor, attempts were made to isolate definite species from the red-brown solutions obtained in the cocondensation reactions of Rh vapour and cyclodienes. Only oily compounds were obtained, which could not be further purified. They strongly interact with chromatographic supports such as alumina, silica, and florisil, and the solutions in the common organic solvents are too unstable to allow isolation of characterizable products. Addition of stabilizing ligands to the cocondensation products has proved to be very useful in obtaining characterizable compounds. When Rh vapour reacts with 1,5-COD, subsequent addition of PPh_3 gives (1,3-η^3-cycloocta-5,6-dienyl)bis(triphenylphosphine)rhodium(I), as a yellow-orange crystalline product, in high yields, and this has been characterized by X-ray analysis [5] (Scheme 2). Such a complex probably arises



SCHEME 2

from a $(1,5\text{-COD})_2Rh^0$ complex, stable at low temperature in excess of ligand, in keeping with observations for the analogous reaction between Co vapour and 1,5-COD [6]. Hydrogen transfer from a diene ligand [7] could account for the formation of the cyclodienyl group on warming to room temperature, while the PPh_3 probably replaces a diene ligand. Thus in the absence of stabilizing ligands (cyclodienyl)(cyclodiene)rhodium(I) complexes could be formed by the metal atom method, and act as catalytic precursors in the hydroformylation of cyclodienes.

The results already obtained, such as the selective hydroformylation of cyclodienes, suggest that cocondensation with atomic metals is very promising as a source of valuable catalysts.

Experimental

Cocondensation reactions. In a typical experiment Rh vapour (40–50 mg) (obtained by resistive heating of tungsten wires surface coated with electrodeposited rhodium) was cocondensed with cyclodienes (10 ml) during 20–30 min (ratio substrate/Rh ca 200 or 270 mol/g.atom) at liquid nitrogen temperature. The flask was warmed to room temperature and toluene (20 ml) was added. The resulting red-brown solution was filtered under nitrogen atmosphere and then used directly in the catalytic hydroformylations.

Hydroformylation runs. The solution from the cocondensation reactions, containing ca. 40 mg of Rh as soluble complex in 10 ml of cyclodiene and 20 ml of toluene, was introduced into a 0.1 l stainless steel autoclave. The vessel was charged with CO/H_2 (1/1) at 70 atm and shaken for two days at room temperature or 50°C depending on the substrate. The products were isolated, and characterized by their mass (Varian MAT-CH7 spectrometer) and ^1H NMR (Varian T60 spectrometer) spectra.

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References

1 P.S. Skell, L.D. Wescott Jr., J.P. Goldstein and R. Engle, J. Amer. Chem. Soc., 87 (1965) 2829; P.L. Timms, Adv. Inorg. Chem. Radiochem., 14 (1972) 12.
2 V.M. Akhmedov, M.T. Antony, M.L.H. Green and D. Young, J. Chem. Soc. Dalton Trans., (1975) 1412; L.H. Simons and J.J. Lagowski, J. Org. Chem., 43 (1978) 3247; W.J. Evans, K.M. Coleson and S.C. Engerer, Inorg. Chem., 20 (1981) 4320; K. Matsuo, K.J. Klabunde, J. Org. Chem., 47 (1982) 843 and refs. therein.
3 G. Vitulli, P. Salvadori, A. Raffaelli, P.A. Costantino and R. Lazzaroni, J. Organomet. Chem., 239 (1982) C23.
4 A. Spencer, J. Organomet. Chem., 124 (1977) 85 and refs. therein.
5 G. Vitulli, A. Raffaelli, P.A. Costantino, C. Barberini, F. Marchetti, S. Merlino and P.S. Skell, J. Chem. Soc. Chem. Comm., (1983) 232.
6 P.L. Timms, T.W. Turney, Adv. Organomet. Chem., 15 (1977) 53.
7 J.R. Blackborow, C.R. Eady, F.W. Grevels, E.A. Koerner Von Gustorf, A. Scrivanti, O.S. Wolfbeis, R. Benn, D.J. Brauer, C. Krüger, P.J. Roberts and Y.H. Tsay, J. Chem. Soc., Dalton Trans., (1981) 661.