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PHOSPHINERHODIUM COMPLEXES AS HOMOGENEOUS CATALYSTS

IX. ASYMMETRIC HYDROGENATION OF AN OLEFIN WITH CATALYSTS FORMED FROM A CHIRAL RHODIUM(I) CARBOXYLATE AND NON-CHIRAL PHOSPHINES *

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Summary

Rhodium carboxylate complexes of the type $[Rh(COD)(OOCR)]_2$ have been prepared and used with phosphines to provide in situ catalysts for olefin hydrogenation. Asymmetric hydrogenation of α-acetamido cinnamic acid methyl ester has been observed using the carboxylate complex prepared from L(+)-mandelic acid. The highest optical yield (13%) was achieved with trimethylphosphine as non-chiral ligand.

Introduction

Rhodium carboxylates have frequently been used as catalysts for the homogeneous hydrogenation of olefins. The complexes known to be catalytically active include $Rh_2(OOCCH_3)_4$ (both in the presence [2] and the absence [3] of a strong acid), $Rh(PPh_3)_3(OOCR)$ R = Me [4,5], Et [4], i-Pr [6], Ph [4], CH_2Cl [4], $CClF_2$ [4], and CF_3 [4]), $Rh(PPh_3)(COD)(OOCPh)$ [7] (COD = 1,5-cyclooctadiene) and $RhH_2(PPh_3)_2(OOCR)$ (R = Ph, PhCH=CH, $PhCH_2CH_2$ and n-C_5H_{11}) [8].

Surprisingly, no efforts have previously been made to use the carboxylato analogues of the useful and variable in situ catalysts based on $[Rh(diene)Cl]_2$ complexes and phosphines. Such systems could be especially interesting for asymmetric hydrogenations [9], since chirality could be incorporated into the catalyst through the phosphine and through the carboxylato ligands. We report below our first results with in situ catalyst systems composed of $[Rh(diene)(OOCR)]_2$ complexes and phosphines.

* For part VIII see Ref. 1.

TABLE 1

IR DATA FOR $[Rh(COD)(OOCR)]_2$ COMPLEXES cm^{-1}, KBr pellets.

RCOO	ν(COO)	ν(OH)
Acetate	1565 1410	—
L(+)-mandelate	1600 1445	3505

Results and discussion

Preparation of rhodium carboxylates

As typefied by Chatt's original synthesis of $[Rh(COD)(OOCCH_3)]_2$ [10], $[Rh(COD)(OOCR)]_2$ complexes are most easily made from $[Rh(COD)Cl]_2$ and a metal salt of the appropriate carboxylic acid. Following Usón [11] we used the Ag salts for this purpose, a benzene solution of $[Rh(COD)Cl]_2$ being treated with the suspended Ag salt. The extent of conversion of the rhodium(I) chloride into the rhodium(I) carboxylate was determined by treating small samples of the benzene solution with CO and recording the IR spectrum in the CO stretching region of the carbonyl complexes so formed. Rhodium carboxylates were prepared in this way from CH_3COOAg and the Ag salt of L(+)-mandelic acid. Table 1 lists IR data for the two rhodium complexes which are in accord with the proposed dimeric, carboxylato-bridged structures.

Hydrogenation of olefins with $[Rh(COD)(OOCCH_3)]_2 + PR_3$ in situ catalysts

The acetatorhodium dimer was found to be an active catalyst for olefin hydrogenation in the presence of alkyl- or aryl-phosphines. Highest rates were achieved with a P/Rh ratio of about 2/1. The in situ systems obtained from $[Rh(diene)Cl]_2$ complexes and phosphines behave similarily [12] and this suggests

TABLE 2

HYDROGENATION OF OLEFINIC SUBSTRATES WITH $[Rh(COD)OOCCH_3)]_2 + PPh_3$ (OR PBu_3) IN SITU SYSTEMS (P/Rh = 2.2/1) OR $Rh(PPh_3)_3Cl$ AS CATALYST

Reaction conditions: rhodium complex (0.025 mmol Rh), phosphine (0.055 mmol) and substrate (2.5 mmol) dissolved in benzene/methanol (1/1) (6 cm^3) at 30°C.

Olefin	$Rh(PPh_3)_3Cl$ catalyst	ITO (min^{-1}) [a]	
		$[Rh(COD)(OOCCH_3)]_2 + PR_3$ catalyst	
		PPh_3	PBu_3
PhCH=CH_2	21	5.4	0.87
E-PhCH=CHCOOH	0.14	0.40	1.4
Fumaric acid	1.3	9.7	38
E-CH_3CH=CHCOOEt	2.7	0.60	0.20
Z-PhCH=C(NHAc)COOMe	2.5	0.48	25

[a] Initial turnover, mol H_2/mol Rh per min.

that the active species formed from the $[Rh(diene)X]_2$ complexes, phosphines and dihydrogen may be of the same type in both cases.

The activity of the catalysts obtained from $[Rh(COD)(OOCCH_3)]_2$ and PPh_3 or PBu_3 for the hydrogenation of several olefins is shown by the data in Table 2. For comparison, the activity of $Rh(PPh_3)_3Cl$ was also determined under the same conditions. The results prove that the in situ catalysts obtained from the acetate complex are comparable to the classical Wilkinson catalyst: for some olefins they are less and for others more active than the latter. The results indicate that the active species formed from these two rhodium complexes must be similar but not identical; they may, for example, be $RhH_2(PR_3)_2Cl$ and $RhH_2(PR_3)_2(OOCCH_3)$ (R = Ph, Bu).

Enantioselective hydrogenation

Rhodium complexes containing chiral phosphines as ligands are extensively used as catalysts for asymmetric hydrogenation [9] but there is little information on the use of other chiral ligands to induce chirality in the product. Some work has been carried out with optically active amides as ligands (and solvents) using $py_2Rh(amide)Cl_2(BH_4)$ complexes as catalysts [13], but the only catalyst for asymmetric hydrogenation containing a chiral carboxylato ligand described previously was the ruthenium complex $RuH(PPh_3)_3$(mandelate) prepared from D(—)-mandelic acid. This latter catalyst, however, shows only low enantioselectivity: 0.4% optical yield was achieved in hydrogenation of 2-ethyl-1-hexene [14].

We tested the chiral rhodium carboxylato complex prepared from L(+)-mandelic acid in the presence of different phosphines for the hydrogenation of α-acetamidocinnamic acid methyl ester, and the results are shown in Table 3. Although

TABLE 3

ENANTIOSELECTIVE HYDROGENATION OF α-ACETAMIDOCINNAMIC ACID METHYL ESTER WITH IN SITU CATALYSTS FORMED FROM $[Rh(COD)(OOCR^*)]_2$ (R*COO = L(+)-MANDELATE) AND VARIOUS PHOSPHINES

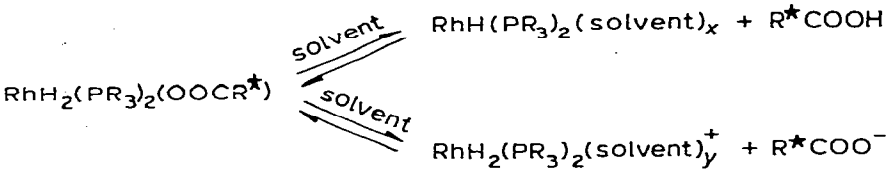
Reaction conditions see Table 2

Phosphine	ITO [a] (min^{-1})	Optical yield (%) [b]	ICP [c] (min^{-1})
PMe_3	1.2	13.0	0.16
PEt_3	24	4.2	1.0
P-n-Pr_3	28	5.9	1.6
P-n-Bu_3	22	4.7	1.0
$P(n\text{-}C_5H_{11})_3$	19	8.1	1.5
$P(n\text{-}C_8H_{17})_3$	24	9.5	2.3
$P(n\text{-}C_{16}H_{33})_3$	9.4	6.6	0.62
P-i-Bu_3	0.17	0 [d]	—
$(Me_2PCH_2)_2$	0.56	0 [d]	—
PPh_3	0.68	0 [d]	—
PPh_2Et	7.2	1.1	0.08
$PPhEt_2$	22	0.8	0.18
$(Ph_2PCH_2CH_2)_2$	20	0 [d]	—

[a] Initial turnover, mol H_2/mol Rh per min. [b] In all cases the D(—)-enantiomer was formed in excess. [c] Initial chiral productivity, mol enantiomeric excess of product/mol chiral component of catalyst per min. [d] Not measurable, less than 0.5%.

the optical yields are not high the in situ catalyst systems based on the rhodium mandelate, especially those formed in the presence of aliphatic phosphines, show definite enantioselectivity; most of the experiments were repeated at least once, and the optical yields were reproduced to within ±1%.

One of the possible explanations of the relatively low optical yields is the loss of the chiral carboxylato group from the catalytically active complex either by reductive elimination of the carboxylic acid or by dissociation of the carboxylate anion



Both these processes would yield catalysts without a chiral ligand and thus lead to lower enantioselectivity. To check this, some hydrogenation experiments were performed in the presence of L(+)-mandelic acid or its Na salt to shift the assumed equilibria back to the left but no increase of the optical yields was observed. Therefore it is probably not the loss of the chiral ligand which causes the low enantioselectivity but rather the fact that only one monodentate chiral ligand is attached to the rhodium atom during the catalytic cycle.

An advantage of some of these new catalysts is their rather high activity: turnovers of about 20 mol H_2/mol Rh per minute were often observed. These catalysts therefore are fairly satisfactory in terms of their "chiral productivity", which we define as the number of moles of chiral molecules produced per mole of chiral catalyst component in unit time.

It is noteworthy that bases such as Et_3N exert a significant influence on the optical yields in hydrogenation of unsaturated carboxylic acids [15]. In view of the results reported above, the formation of rhodium carboxylates must be regarded as a possible explanation of this effect.

Experimental

[Rh(1,5-cyclooctadiene)Cl]$_2$ was prepared by the method of Chatt and Venanzi [10]. P-n-Bu_3 and PPh_3 were purchased from Fluka, $Me_2PCH_2CH_2PMe_2$ was kindly supplied by R.B. King (University of Georgia, Athens, U.S.A.) and the following phosphines were prepared by the published procedures: trialkyl phosphines [16], $PPhEt_2$ [17], PPh_2Et [17] and $Ph_2PCH_2CH_2CH_2PPh_2$ [18]. The purity of the compounds was checked by GLC (5% SE-30 on Chromosorb W) or phosphorus analysis.

[Rh(COD)(L-mandelate)]$_2$

100 mg (0.21 mmol) [Rh(COD)Cl]$_2$ and 130 mg (0.5 mmol) of L(+)-mandelic acid silver salt (pulverized) were stirred in 50 ml benzene under argon. Every 2 h a small sample was taken from the liquid phase of the mixture (which is a slurry because of the unsoluble silver salts) and treated with CO. A rapid colour change of this sample from yellow to red indicated the transformation of the COD com-

plexes to the carbonyl derivatives. The infrared spectrum of this solution in the CO stretching region was used to check the extent of conversion of $[Rh(COD)Cl]_2$ into $[Rh(COD)(OOCCH(OH)C_6H_5)]_2$. The CO streching vibrations (cm^{-1}) of $[Rh(CO)_2Cl]_2$ and $[Rh(CO)_2(OOCCH(OH)C_6H_5)]_2$ in benzene are shown below.

$[Rh(CO)_2Cl]_2$	$[Rh(CO)_2(OOCCH(OH)C_6H_5)]_2$
2035vs	2029vs
2090vs	2079m
2106m	2101s

When the IR spectra no longer showed the presence of $[Rh(CO)_2Cl]_2$, and accordingly all the $[Rh(COD)Cl]_2$ had reacted, the mixture was filtered, concentrated in vacuo to a few ml, and the rhodium carboxylate precipitated by the addition of n-heptane. Filtering and washing with n-heptane gave the [Rh(COD)-(L-mandelate)]$_2$ as orange crystals in 90%. Anal. Found: C, 52.8; H, 5.3; Rh, 28.5; mol.wt., 750 ± 15. $C_{32}H_{38}O_6Rh_2$ calcd.: C, 53.05; H, 5.28; Rh, 28.42%; mol.wt. 724.4

$[Rh(COD)(OOCCH_3)]_2$

This compound was prepared analogously from $[Rh(COD)Cl]_2$ and CH_3COOAg. Anal.: Found: C, 44.1; H, 5.8. Calcd.: C, 44.46: H, 5.59%.

Hydrogenation experiments

0.0125 mmol [Rh(COD)(OOCR)] complex and 0.055 mmol monotertiary phosphine (or 0.0275 mmol ditertiary phosphine) were dissolved under Ar in 3 ml benzene and 0.5 ml methanol contained in a thermostatted flask which was connected to a thermostatted gas burette and equipped with a magnetic stirrer and a silicone rubber cap. After prehydrogenation for 30 min 2.5 mmol (548 mg) *Z*-α-acetamidocinnamic acid methyl ester dissolved in 2.5 ml methanol was added from a syringe. Hydrogenation was followed by measuring the gas consumption. Complete reaction took from a few minutes to 24 h, depending on the phosphine used.

When the reaction was complete the solvent was removed in vacuum and the product chromatographed on a silica gel column and eluted with hexane/ethyl acetate. The resulting products were colourless or faintly yellow, indicating essentially complete removal of the catalyst. The optical rotations of the products were measured in chloroform on a Schmidt Haensch LM visual polarimeter with an accuracy of approximately 0.01°.

If added L(+)-mandelic acid or its Na salt were used in the hydrogenation the chromatographed product was dissolved in chloroform, the solution extracted several times with water, and then the solvent again removed in vacuum. Control experiments confirmed that this method removed all the free L(+)-mandelic acid from the product.

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References

1 S. Törös, B. Heil and L. Markó, J. Organometal. Chem., 159 (1978) 401.
2 P. Legzdins, R.W. Mitchell, G.L. Rempel, J.D. Ruddick and G. Wilkinson, J. Chem. Soc. (A), (1970) 3322.
3 B.C.Y. Hui, W.K. Teo and G.L. Rempel, Inorg. Chem., 12 (1973) 757.
4 R.W. Mitchell, J.D. Ruddick and G. Wilkinson, J. Chem. Soc. (A), (1971) 3224.
5 A. Spencer, J. Organometal. Chem., 93 (1975) 389.
6 G. Sbrana, G. Braca, G. Valentini, G. Pazienza and A. Altomare, J. Mol. Catal., 3 (1977/78) 111.
7 R.H. Crabtree, A. Gautier, G. Giordano and T. Khan, J. Organometal. Chem., 141 (1977) 113.
8 Z. Nagy-Magos, B. Heil and L. Markó, Transition Met. Chem., 1 (1976) 215.
9 L. Markó and B. Heil, Catalysis Reviews, 8 (1975) 269; J.D. Morrison, W.F. Masler and M.K. Neuberg, Adv. Catal., 25 (1976) 81.
10 J. Chatt and L.M. Venanzi, J. Chem. Soc., (1977) 4735.
11 R. Usón, L.A. Oro and F. Ibanez, Rec. Acad. Cienc. Exactas, Fis.-Quim. Nat. Zaragoza, 30 (1975) 169.
12 L. Horner and H. Siegel, Liebigs Ann. Chem., 751 (1971) 135.
13 P. Abley and F.J. McQuillin, Chem. Commun., (1969) 477; J. Chem. Soc. (C), (1971) 844.
14 G. Sbrana, G. Braca and E. Giannetti, J. Chem. Soc. Dalton Trans., (1976) 1847.
15 K. Achiwa, Chem. Lett., (1978) 561; I. Ojima, T. Kogure and K. Achiwa, Chem. Lett., (1978) 567; G. Descotes, D. Lafont and D. Sinou, J. Organometal. Chem., 150 (1978) C14.
16 W.C. Davies, J. Chem. Soc., (1933) 1043.
17 J. Meisenheimer, Ann., 449 (1926) 213.
18 K. Issleib and H.O. Fröhlich, Z. Naturforsch., 14b (1959) 349.