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RHODIUM- AND PLATINUM-CATALYZED ASYMMETRIC HYDROFORMYLATION WITH (2*S*,3*S*)-2,3-BIS(DIPHENYLPHOSPHINO)BUTANE AS THE CHIRAL LIGAND *

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Summary

Some mono- and disubstituted ethenes have been asymmetrically hydroformylated with rhodium and platinum catalysts using (2*S*,3*S*)-2,3-bis(diphenylphosphino)butane (Chiraphos) as the chiral ligand (maximum optical yield ~ 45%). The results are compared with those obtained when the chiral ligand is (4*R*,5*R*)-2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane (Diop). The Chiraphos ligand causes a decrease of the catalytic activity with respect to Diop. Optical yields for rhodium catalysts are always higher with Chiraphos, whereas scattered results were obtained with platinum catalysts. Since for the catalytic systems examined asymmetric induction takes place before or during the formation of the intermediate diastereomeric metal alkyl complexes, the results are tentatively rationalized on the basis of a stereochemical model for the transition state leading to the above metal alkyl complexes intermediate.

Introduction

In spite of the very large number of chiral phosphine ligands used in homogeneous asymmetric catalysis by transition metal complexes [1,2] very few of them have been employed in asymmetric hydroformylation [3]. In most of the cases either 2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane (Diop) or related chelate ligands have been used [3–7].

In order to investigate the possible role of the size and of the conformational mobility [8–10] of the ring formed by chelation of a diphosphine ligand to the metal

* Dedicated to Prof. J. Halpern on the occasion of his 60th birthday.

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TABLE 1

HYDROFORMYLATION OF SOME OLEFINS WITH RHODIUM CATALYTIC SYSTEMS IN THE PRESENCE OF EITHER (*S,S*)-Chiraphos OR (*R,R*)-Diop [a]

Substrate	$[Rh(NBD)Cl]_2$ [b] + (*S,S*)-Chiraphos		$HRh(CO)(PPh_3)_3$ [c] + (*R,R*)-Diop	
	Reaction time (h)	Conversion [e] to aldehyde (%)	Reaction time (h)	Conversion [e] to aldehydes (%)
1-Butene	6	35	3 [d]	70
(*Z*)-2-butene	72	55	22 [d]	30
(*E*)-2-butene	97	40	22 [d]	25
2,3-Dimethyl-1-butene	168	43	96	82
Styrene	3	80	1	94
2-Phenylpropene	70	30	46	77
Bicylo[2.2.1]-2-heptene	3	~100	1	~100

[a] Reaction conditions: T 100 °C (unless otherwise stated); $p_{CO} = p_{H_2} = 40$ atm, L–L/Rh = 4/1. [b] $\sim 2 \times 10^{-3}$ mol l^{-1}. [c] $\sim 2.5 \times 10^{-3}$ mol l^{-1}. [d] Reaction temperature 95 °C. [e] [Mol aldehydes/mol substrate (initial)] × 100.

on the stereochemical control in asymmetric hydroformylation we have pursued our investigation in this field [6] using diphosphines which give five membered (and therefore more rigid) rings [11–17] upon coordination as the chiral ligand. In the present paper we compare the results of the asymmetric hydroformylation of different types of olefinic hydrocarbons by using either a Pt/(*S,S*)-Chiraphos or a Rh/(*S,S*)-Chiraphos catalytic system (Chiraphos = 2,3-bis(diphenylphosphino)-butane [11]) with the results previously obtained using (*R,R*)-Diop as the chiral ligand.

Results and discussion

In the platinum-catalyzed hydroformylation the experiments were carried out using as the catalyst precursor the complex [(*S,S*)-Chiraphos]PtCl($SnCl_3$) prepared from [(*S,S*)-Chiraphos]$PtCl_2$ [18] and $SnCl_2$. In CH_2Cl_2 solution at −45 °C partial dissociation of $SnCl_2$ is indicated (~ 10%) by ^{31}P NMR spectroscopy.

For rhodium-catalyzed hydroformylation experiments, the catalyst was prepared in situ from $[Rh(NBD)Cl]_2$ and (*S,S*)-Chiraphos with a Chiraphos/Rh molar ratio of 4.

As standard conditions for the reactions $p_{CO} = p_{H_2} = 40$ atm and 100 °C were used.

(a) Hydroformylation experiments

A remarkable decrease in the activity of the catalyst has been noticed in all cases when Chiraphos was substituted for Diop (Tables 1 and 2) *. Furthermore, using

* The type of catalyst precursor used does not influence significantly regio- and stereoselectivity of hydroformylation when optically active ligand to metal ratios are used for which a limit value of the optical yield is reached [19,20]. This ratio is 4 in the case of Chiraphos and 2 in the case of Diop [20]. The results reported in the tables are therefore comparable, even if different catalytic catalyst precursors are used. We are thankful to the referee who brought up this point.

Chiraphos a very large increase in induction period has been noticed for the platinum-catalyzed reactions whose origin has not been investigated. With all catalytic systems, except for the Pt/Diop, hydroformylation is more rapid with olefins having a phenyl group bound to a carbon atom of the double bond than with aliphatic terminal olefins having the substituent in the same position. With the rhodium catalytic systems norbornene reacts more rapidly than any other olefin tested, but in the case of platinum/Diop catalytic system it reacts more slowly than the other substrates investigated.

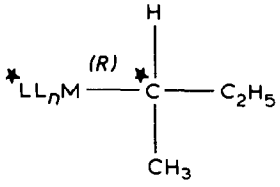
With the possible exception of styrene, the platinum/Diop catalytic systems are more active than the corresponding rhodium ones. The differences are larger for the 1,1-disubstituted ethenes than for the monosubstituted ethenes. However, the opposite is true for the Chiraphos-containing catalytic systems (Tables 1 and 2).

It is known [21] that the selectivity for formation of aldehydes is high with the rhodium catalytic systems. With platinum, hydrogenation of the olefins accompanies the hydroformylation; the extent of hydrogenation is in general similar with Chiraphos and Diop. Hydrogenation is faster with terminal olefins than with internal olefins.

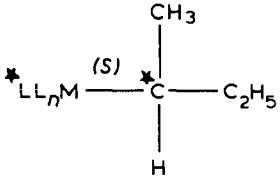
Double bond shift in the substrate is particularly evident in the case of the hydroformylation of internal olefins where it can be detected from the amount of linear aldehyde produced. As can be deduced from Table 3 the double bond shift occurs only with platinum catalysts and it is greater in Diop- than in Chiraphos-containing catalytic systems.

(b) Identification of the step mainly influencing regioisomeric and enantiomeric composition of the hydroformylation products

2-Methylbutanal obtained from 1-butene and from (*Z*)- and (*E*)-2-butene has opposite prevailing chirality both when Rh/Chiraphos and Pt/Chiraphos catalytic systems are used. Therefore, in both cases, as with the corresponding Diop systems [3,6] asymmetric induction takes place during or before the formation of the diastereomeric metal alkyl complexes **A** and **B**,



(A)



(B)

which are assumed [22,23] to be intermediates in the catalytic cycle.

As in a previous paper [3], we assume that the transition state that controls the enantiomeric excess in the catalytic cycle is the one leading to the formation of the two diastereomeric metal alkyl complexes from the corresponding hydridometal olefin complexes. This step has been shown [24,25] to be largely irreversible.

A simplified planar representation of the above transition state is depicted in Fig. 1 and has been discussed in detail in a previous paper [3]. Depending on the quadrants occupied by the group(s) bound to the carbon atoms of the olefinic

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TABLE 2

HYDROFORMYLATION OF SOME OLEFINS USING EITHER [(*S*,*S*)-Chiraphos]Pt($SnCl_3$)Cl OR [(*R*,*R*)-Diop]Pt($SnCl_3$)Cl [a]

Substrate	[(*S*,*S*)-Chiraphos]Pt($SnCl_3$)Cl [c]				[(*R*,*R*)-Diop]Pt($SnCl_3$)Cl [b]			
	Induction time (h)	Reaction time (h)	Conversion [d] (%)	Selectivity [e] to aldehydes (%)	Induction time (h)	Reaction time (h)	Conversion [d] (%)	Selectivity to aldehydes (%)
1-Butene	12	10	36	72	0.1	0.42	63	49
(*Z*)-2-butene	100	25	14	~100	0.3	0.42	26	92
(*E*)-2-butene	24	46	19	~100	0.3	0.58	24	92
2,3-Dimethyl-1-butene	30	62	38	79	0	4.0	62 [f]	85
Styrene	12	9	47	74	0	0.90	70	73
2-Phenylpropene	15	48	65	26	0	4.0	86	77
Bicyclo[2.2.1]-2-heptene	46	50	n.d.	n.d.	0.5	3.5	37 [f]	n.d.

[a] Reaction conditions *T* 100 °C (unless otherwise stated); $p_{CO} = p_{H_2} = 40$ atm. [b] 1.68×10^{-3} mol l^{-1}. [c] 2.25×10^{-3} mol l^{-1}. [d] [Mol reacted substrate/mol substrate(initial)]×100. [e] [Mol aldehydes/mol reacted substrate]×100. [f] Reaction temperature 80 °C.

TABLE 3

REGIO- AND ENANTIOSELECTIVITY IN HYDROFORMYLATION CATALYZED BY RHODIUM OR PLATINUM IN THE PRESENCE OF EITHER Diop OR Chiraphos AS THE CHIRAL LIGAND (s.c. = straight chain isomer; b = branched isomer o.p. = optical purity (in %))

Substrate	(*S*,*S*)-Chiraphos				(*R*,*R*)-Diop			
	(L–L)Pt($SnCl_3$)Cl		$Rh(NBD)Cl_2$		(L–L)Pt($SnCl_3$)Cl		$RhH(CO)(PPh_3)_3$	
	isomer ratio s.c./b.	o.p.	isomer ratio s.c./b.	o.p.	isomer ratio s.c./b.	o.p.	isomer ratio s.c./b.	o.p.
1-Butene	91/9	40.0 (*S*)	54/46	7.1 (*R*)	94/6	24.8 (*R*)	92/8	5.9 (*R*)
(*Z*)-2-butene	28/72	23.1 (*R*)	0/100	18.4 (*S*)	45/55	7.7 (*S*)	0/100	8.0 (*S*)
(*E*)-2-butene	31/69	8.8 (*R*)	1/99	18.5 (*S*)	49/51	13.4 (*S*)	0/100	3.2 (*S*)
2,3-Dimethyl-1-butene	100/0	19.8 (*S*)	100/0	21.8 (*R*)	100/0	15.0 (*R*)	100/0	3.5 (*S*)
Styrene	38/62	45.0 (*R*)	6/94	24.2 (*R*)	62/38	4.4 (*S*)	29/71	10.0 (*R*)
2-Phenylpropene	99/1	3.0 (*S*)	99/1	21.4 (*R*)	100/0	7.2 (*S*)	100/0	1.4 (*R*)
Bicyclo[2.2.1]-2-heptene	*exo*	8.3 [a]	*exo*	16.4 [a]	*exo*	29.2 [a]	*exo*	3.3 [b]

[a] (1*R*,2*R*,4*S*). [b] (1*S*,2*S*,4*R*).

double bond (Fig. 1), different repulsive interactions between olefinic substrate and catalyst can be envisioned. Their magnitude will determine the relative energy of the possible transition states, and determine the direction and extent of enantiomeric and regioisomeric excess [3].

Possible electronic and/or attractive interactions are not considered in this model. The relative size of L′ and L″ for the different catalytic systems (Fig. 1) is determined on the basis of the prevailing antipode obtained in the hydroformylation of a test substrate (e.g., (*Z*)-2-butene).

(c) Regioselectivity

Since no internal C_5 olefins have been investigated, only the regioselectivity for terminal olefins can be discussed on the basis of the present results. For 1,1-disubstituted ethenes addition of the formyl group at the terminal $=CH_2$ groups largely prevails (98% or more) in agreement with the stereochemical model we have proposed (Fig. 1, $Z \gg H$). We have not attempted to determine exactly the very small amount of other regioisomers which are present in the reaction products although a careful determination of the isomeric excess, which in this case is comprised between 98 and 100%, would be of interest. In fact, according to our model the isomeric excess gives an indication, at least for aliphatic substrates, of the order of magnitude of the sum of the steric repulsions in quadrants (1) and (2) with respect to that in quadrants (−1) and (−2) (Fig. 1).

For monosubstituted ethylenes, both with the Pt- and with the Rh-catalytic systems a lower amount of the linear isomer is obtained in the hydroformylation of 1-butene when Chiraphos is used instead of Diop. The difference is much larger with the rhodium than with the platinum catalysts.

Styrene behaves in a different manner when compared with 1-butene in that it gives much less linear isomer with all catalytic systems used. In three cases the results are in contrast with the predictions (Table 4) of the stereochemical model which considers only steric interactions. The failures of the model to predict the prevailing regioisomer may originate in the fact that the energy of the transition state, in which the carbon atom of the olefinic bond bearing the phenyl group is nearer to the metal atom, is lower than that of the transition state in which $=CH_2$ approaches the metal atom. This situation seems reasonable in view of the well-known large polarisability [26] of the phenyl group.

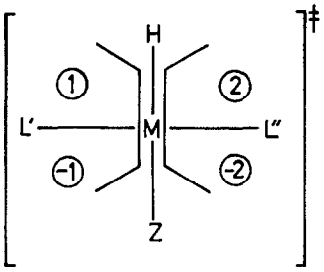

Fig. 1 Model for the transition state in which regio- and stereoisomeric excess is determined. L′ and L″ = large and small ligand resp. for Rh/Diop, Pt/Diop, Rh/Chiraphos; L′ and L″ = small and large ligand resp. for Pt/Chiraphos Z = ligand different from hydrogen

TABLE 4

COMPARISON BETWEEN EXPERIMENTS AND PREDICTIONS BY THE STEREOCHEMICAL MODEL (Fig. 1) FOR THE UNSATURATED CARBON ATOM PREVAILINGLY FORMYLATED AND FOR THE ABSOLUTE CONFIGURATION OF THE CHIRAL REACTION PRODUCT IN ASYMMETRIC HYDROFORMYLATION [a]

(Metal component of the catalyst: rhodium or platinum; asymmetric ligand: (*S*,*S*)-Chiraphos or (*R*,*R*)-Diop. Size of L′ and L″ in the model determined from the results of (*Z*)-2-butene asymmetric hydroformylation)

Substrate	(*S*,*S*)-Chiraphos								(*R*,*R*)-Diop							
	Rh				Pt				Rh				Pt			
	A		B		A		B		A		B		A		B	
	P	F	P	F	P	F	P	F	P	F	P	F	P	F	P	F
1-Butene	1	1	(*R*)	(*R*)	1	1	(*S*)	(*S*)	1	1	(*R*)	(*R*)	1	1	(*R*)	(*R*)
(*Z*)-2-butene		2	(*S*)	(*S*)		2	(*R*)	(*R*)		2	(*S*)	(*S*)		2	(*S*)	(*S*)
(*E*)-2-butene		2		(*S*)		2		(*R*)		2		(*S*)		2		(*S*)
2,3-Dimethyl-1-butene	1	1	(*R*)	(*R*)	1	1	(*S*)	(*S*)	1	1	(*R*)	(*S*)	1	1	(*R*)	(*R*)
Styrene [b]	1	2	(*R*)	(*R*)	1	2	(*S*)	(*R*)	1	2	(*R*)	(*R*)	1	1	(*R*)	(*S*)
2-Phenylpropene	1	1	(*R*)	(*R*)	1	1	(*S*)	(*S*)	1	1	(*R*)	(*R*)	1	1	(*R*)	(*S*)
Bicyclo[2.2.1]-2-heptene		2	(1*R*..)	(1*R*..)		2	(1*S*..)	(1*S*..)		2	(1*R*..)	(1*S*..)		2	(1*R*..)	(1*R*..)

[a] A = Unsaturated carbon atom prevailingly formylated. B = Prevailing antipode in the chiral isomer. P = Predicted. F = Found. [b] To obtain a consistent comparison with aliphatic olefins the olefinic carbon atoms of styrene are numbered as follows: $\overset{1}{CH_2}=\overset{2}{CH}-Ph$.

(d) Enantioselectivity

As shown in Table 3 for the rhodium-catalyzed hydroformylation when Chiraphos is used instead of Diop, the same prevailing chirality is obtained with 1-butene, (*Z*)- and (*E*)-2-butene, styrene and 2-phenylpropene. In contrast, the opposite prevailing chirality is found with the two ligands using 2,3-dimethyl-1-butene and norbornene. In all cases the observed enantiomeric excess (e.e.) is larger using Chiraphos instead of Diop. With platinum catalytic systems the opposite prevailing chirality is obtained when Chiraphos or Diop is used as the chiral ligand with two exceptions (2-phenylpropene and norbornene). The observed e.e.'s are higher using Chiraphos than using Diop for 1-butene, 2,3-dimethyl-1-butene and styrene but lower for 2-phenylpropene and norbornene. The comparison is not meaningful in the case of (*Z*)- and (*E*)-2-butene because of the different extent of isomerisation of the substrates due to hydrogen shift.

As shown in Table 4 no exceptions to the prediction based on the model have been found for the Rh/Chiraphos system. Only substrates with an aromatic ring directly bound to the double bond give results in contrast to the predictions for Pt/Chiraphos and Pt/Diop catalytic systems. Furthermore, only in the case of the Rh/Diop have wrong predictions been obtained with two substrates not containing aromatic rings (norbornene and 2,3-dimethyl-1-butene), the e.e being less than 4% in both cases.

For the Pt/Chiraphos catalytic system a similar enantiomeric excess but opposite chirality is observed in the branched hydroformylation products of 1-butene and styrene. Although no change in prevailing chirality occurs, a substantial decrease in e.e. is observed when 2,3-dimethyl-1-butene and 2-phenylpropene hydroformylation products are compared. Both for styrene and 2-phenylpropene a change in the chirality has been noticed with the Pt/Diop catalytic system in comparison to the results obtained in the hydroformylation of 1-butene and 2,3-dimethyl-1-butene, respectively.

A possible interpretation of these failures of the model involves the assumption of the existence of attractive interactions, not considered in the model, between the phenyl group of the substrate and a phenyl group of the ligand or the metal atom present in the catalytic complex.

These attractive interactions should occur for the catalytic system Pt/Chiraphos in quadrant (−2) and in quadrant (+2) and for the catalytic system Pt/Diop in quadrant (+1) and in quadrant (−1).

From the differences in the extent of the enantiomeric excess between aliphatic and aromatic substrates these interactions should vary between 100 and 1300 cal mol^{-1}. Such weak interactions between phenyl groups in non-polar solvents have been already observed [27,28].

Conclusions

The extent of asymmetric induction in hydroformylation brought about by Chiraphos in platinum or rhodium catalytic systems is much lower than that observed in the hydrogenation of acylaminoacrylic derivatives [11] but comparable and even higher than that observed in the hydrogenation of non-functionalized olefins. The Chiraphos chiral ligand gives larger e.e.'s than Diop with the rhodium catalytic systems as expected [11,12]. However, this is not true for platinum catalytic systems.

Since the catalytic step controlling the enantiomeric excess with Chiraphos is the same as with Diop, the stereochemical model for the transition state proposed for Diop can be used to rationalize both the regio- and enantioselectivity data observed with Chiraphos. As usual, the success of a stereochemical model does not help in defining the structure of a catalytic intermediate and does not provide per se further evidence concerning the catalytic mechanism. However, in this case the step determining the enantiomeric excess is proved by independent experiments [3], and this allows us to formulate a reasonable model of the transition state involved in the above step (independent of the structure of the chiral ligand).

Experimental

GLC analysis (2 m × 0.29 cm columns packed with 15% Carbowax 20 M on Chromosorb W 80–100 mesh, silicon oil 2% GE SF-96 on Chromosorb B 80–100 mesh, and polypropylenglycol 15% on Chromosorb G 80–100 mesh and 4 m × 0.29 cm column packed with 25% dimethylsulfolane on Kieselgur 60–100 mesh) were performed on a Perkin–Elmer Sigma 4 gaschromatograph with flame ionization detector. ^{1}H NMR spectra were recorded on a Bruker WH 90 spectrometer using TMS as the internal standard. ^{31}P NMR spectra were recorded on the same instrument using H_3PO_4 as the external standard. Optical rotations were measured with a Perkin–Elmer polarimeter 141. Mass spectra were run on a Hitachi/Perkin–Elmer RMU-6L spectrometer. IR spectra were recorded on a Perkin–Elmer 325 spectrometer.

(2*S*,3*S*)-2,3-bis(diphenylphosphino)butane (Chiraphos) [11], [(*S*,*S*)-Chiraphos]-$PtCl_2$ [18] and $[Rh(NBD)Cl]_2$ [29] were prepared according to methods already described in the literature. Ethylbenzene (used as the solvent for hydroformylation of the linear butenes) and benzene were distilled under nitrogen on sodium and $LiAlH_4$, respectively. CH_2Cl_2 was distilled on CaH_2 under nitrogen. Olefinic substrates were Fluka products.

Synthesis and characterization of PtCl(SnCl$_3$)(Chiraphos) (I)

I was synthesized reacting $PtCl_2$(Chiraphos) (II) in CH_2Cl_2 for 5 h with a small excess of $SnCl_2$, as described in the literature for the Diop analogue [30]. After filtration of the unreacted $SnCl_2$, hexane was added to the solution and I crystallized. After drying, I was dissolved in CH_2Cl_2 and reacted for further 2 h with 1 equiv. $SnCl_2$. The unreacted $SnCl_2$ was filtrated and I crystallized through slow evaporation of the solvent. Yield 50%. IR (Nujol): 350m and 338s cm^{-1} (ν($SnCl_3$)) and 330sh cm^{-1} (ν(Pt–C)) [31]. No trace of II (signals at 320 and 290 cm^{-1} ν(Pt–Cl)) was detectable.

^{31}P NMR (−45 °C, CD_2Cl_2): δ 49.5 ppm, P *trans* Sn, ^1J(Pt–P) 2917, ^2J(P–P) 13.4 Hz; 39.8 ppm, P *trans* Cl, ^1J(Pt–P) 3244, ^2J(P–P) 13.4 Hz.

Also the signals of II [18] (I/II ca. 10/1 molar ratio) were recognizable.

Hydroformylation procedure

Platinum-catalyzed hydroformylation. 40 mg (4.54×10^{-5} mol) of PtCl($SnCl_3$)-(Chiraphos) were put into the autoclave. The autoclave was evacuated and cooled at 0 °C. 10 ml olefin (0.08–0.10 mol depending on the olefin used) were condensed or weighted in a Schlenk-type flask, 10 ml of an aromatic solvent (benzene or

ethylbenzene) were added and the mixture was sucked into the autoclave. 80 atm of an equimolar mixture of CO and H_2 were pressurized and the autoclave was placed into an oil bath at 100 °C. After the desired conversion was reached (evaluated from the decrease of the pressure) the autoclave was cooled, depressurized and opened.

Conversion, chemo- and regioselectivity were determined directly on the reaction products through GLC using the solvent as internal standard. This solution was than fractionated and the quantity of aldehyde necessary for measuring the optical rotation was isolated.

Rhodium-catalyzed hydroformylation. The procedure was similar to that used for the platinum catalyst except for the quantities used. The catalysts was formed in situ from 16.8 mg of $[Rh(NBD)Cl]_2$ and 122.6 mg of (*S*,*S*)-Chiraphos in 36 ml of solvent. 0.1 mol of substrate were used.

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