JOURNAL OF CATALYSIS 87, 517–519 (1984)

Catalytic Ability of Cobalt(II) and Nickel(II) Chiral Diphosphine Complexes for Asymmetric Hydrogenation of Prochiral Unsaturated Esters

INTRODUCTION

Successful development in asymmetric homogeneous hydrogenation of olefins catalyzed by chiral rhodium(I) complexes has made possible to give excellent enantioselectivity, in the case of α-(acylamino)cinnamic acid and its derivatives enantiomeric excess over 95% has been attained (*1*). Nevertheless, chiral first-row transition metal complexes, which have been the subject of only limited investigation in the asymmetric hydrogenation (*2, 3*), are also required in a viewpoint of practical asymmetric synthesis of optically active compounds.

In this paper, we describe the catalytic features of Co(II) and Ni(II) chiral diphosphine complexes for the asymmetric hydrogenation of prochiral unsaturated esters.

METHODS

Materials. (−)-2,3-*O*-Isopropylidene-1,4-bis(diphenylphosphino) - 2,3 - butanediol (DIOP) was synthesized by Kagan's method (*4*). The isolable cobalt complex, $CoCl_2$((−)-DIOP), was prepared by refluxing the ethanolic solution (30 cm^3) of $CoCl_2$ (2 g) and (−)-DIOP (1.5 g) for 2 h in a nitrogen atmosphere; the blue-crystal complex separated on cooling at 0°C: mp 207–213°C; ir (CsI): 308 and 345 cm^{-1} (CoCl). Anal. calcd for $C_{31}H_{32}O_2P_2Cl_2Co$: C, 59.25%; H, 5.14%; M, 627. Found: C, 59.09%; H, 5.14%; M^+, 627. The nickel complex, $NiCl_2$((−)-DIOP), was prepared in a similar manner, noncrystallizing from the solution on cooling, the ethanolic solution was evaporated to dryness. The resulting solid was washed with ether and dissolved in benzene. The solution was filtered, and then evaporated to give pale-yellow crystals: mp 165–173°C (dec.); ir (CsI): 308 cm^{-1} (broad, NiCl). Anal. calcd for $C_{31}H_{32}O_2P_2Cl_2Ni$: C, 59.27%; H, 5.14%; M, 626. Found: C, 57.63%; H, 5.66%; a molecular ion was undetectable.

Reaction procedure and analysis. The hydrogenation of prochiral esters (2 cm^3) with the chiral Co(II) or Ni(II) complex (0.16 mmol) was carried out in an autoclave under initial H_2 pressure of 50 Kg/cm^2. The reaction mixture was hydrolyzed by refluxing in 10% NaOH–methanol solution to obtain the saturated acid, which was supplied to the measurement of the optical rotation. The product was identified and determined by ^1H NMR and GLC.

RESULTS AND DISCUSSION

The Co(II)– and Ni(II)–(−)-DIOP complexes isolated or prepared *in situ* were able to catalyze the hydrogenation of unsaturated esters such as methyl or ethyl α-methylcrotonate slowly at 80–100°C, but had no catalytic ability for the reduction of the carbon–carbon double bond in bulky unsaturated acid and esters such as α-(acetylamino)cinnamic acid derivatives, which have led to high enantioselectivity in the chiral Rh(I)-complex-catalyzed hydrogenation (*1*).

In Table 1, results in the hydrogenation of ethyl α-methylcrotonate by Co(II)– and Ni(II)–(−)-DIOP complexes with or without Et_3N at 80–100°C are summarized. Although in both the Co(II)- and Ni(II)-complex-catalyzed reactions without Et_3N the rates were extremely low, addition of the

0021-9517/84 $3.00

TABLE 1

Asymmetric Hydrogenation of Ethyl α-Methylcrotonate by Transition Metal–(−)-DIOP Complexes with or without Triethylamine

Catalytic system[a]	Temp. (°C)	Time (h)	Yield (%)	e.e.[b] (%)
$CoCl_2$/(−)-DIOP	100	96	20	3.6(*R*)
$CoCl_2$/(−)-DIOP	80	22	Trace	n.d.
$CoCl_2$/(−)-DIOP + Et_3N	80	22	5	7.4(*R*)
$CoCl_2$/(−)-DIOP + 2 Et_3N	80	22	17	11.7(*R*)
$CoCl_2$/(−)-DIOP + 4 Et_3N	80	22	9	0.8(*R*)
$CoCl_2$/(−)-DIOP + 2 (+)-$PhCH(Me)NH_2$	80	22	6	9.3(*S*)
$CoCl_2$((−)-DIOP) + 2 Et_3N	80	22	6	11.5(*R*)
$NiCl_2$/(−)-DIOP	80	22	Trace	n.d.
$NiCl_2$/(−)-DIOP + 2 Et_3N	80	22	12	8.4(*R*)
$NiCl_2$((−)-DIOP) + 2 Et_3N	80	22	7	10.0(*R*)
$[Rh(C_2H_4)_2Cl]_2$/(−)-DIOP	25	72	38	1.7(*R*)
Ru_2Cl_4((−)-DIOP)$_3$	50	32	20	2.7(*R*)
Ru_2Cl_4((−)-DIOP)$_3$ + Et_3N	50	22	39	2.6(*R*)
Ru_2Cl_4((−)-DIOP)$_3$ + 2 Et_3N	50	22	29	7.5(*R*)

[a] The catalytic system expressed as MCl_2/(−)-DIOP + *n* Et_3N (*M* = Co or Ni) indicates a mixture of *in situ* prepared Co(II)- or Ni(II)–(−)-DIOP complex ([MCl_2] = [(−)-DIOP] = 0.16 mmol) and Et_3N (*n* × 0.16 mmol).

[b] Values of e.e. were determined with regard to α-methylbutyric acid; $[\alpha]_D^{24}$ + 12.17° (*c* = 5.12, in C_2H_5OH) for the (*S*)-acid (*5*). Configuration in parentheses.

amine to the reaction systems resulted in the enhancement of the hydrogenation rate and the enantiomeric excess (e.e.) of the product. The maximum e.e. of 11.7% was obtained in the reaction system of *in situ* prepared Co(II)–(−)-DIOP and Et_3N (Co/Et_3N = ½). It has been also shown that the addition of a small amount of Et_3N to the reaction system increases the enantioselectivity in the asymmetric hydrogenation of olefinic acids such as α-(acetylamino)cinnamic acid by rhodium(I) chiral phosphine complexes (*6*). This enhancement has been proposed to be attributable to favorable alternation in the predominant reaction pathway for the effective asymmetric induction due to the generation of the carboxylate anion of the free substrate by the addition of the amine, however no effects of added amine for the ester of methyl α-(acetylamino)cinnamate have been observed (*6*). Therefore, the observed effects of added Et_3N on the rate and the enantioselectivity in the present reaction may be due to improvement of the stereochemistry requirement in the coordination sphere of the chiral complex. Presumably, the addition of Et_3N induces the formation of catalytically active species, expressed as HMCl((−)-DIOP) (Et_3N) (*M* = Co or Ni), as

$$MCl_2((-)\text{-DIOP}) + Et_3N + H_2 \rightleftharpoons HMCl((-)\text{-DIOP}) + Et_3NHCl$$

$$HMCl((-)\text{-DIOP}) + Et_3N \rightleftharpoons HMCl((-)\text{-DIOP})(Et_3N)$$

where *M* indicates Co(II) or Ni(II). The putative complex of HMCl((−)-DIOP)(Et_3N) probably exhibits the enantio-face selection of the prochiral substrate more efficiently than MCl_2((−)-DIOP) *per se* during π-complex formation between HMCl((−)-DIOP)(Et_3N) and the substrate. In this regard, the use of a bulky chiral amine, (+)-$C_6H_5CH(CH_3)NH_2$, instead of Et_3N decreased the reaction rate and the enantioselectivity, but resulted in the change of the prevailing configuration of the product from (*R*)-enantiomer to antipode, indicating that the chirality of the adduct affected the asymmetric induction of the catalyst. However, the excess of Et_3N ($Et_3N/MCl_2 > 2$) decreased the rate and the selectivity considerably.

It is also noteworthy that the enantioselectivities of MCl_2-(−)-DIOP (*M* = Co or Ni) are higher than those of Rh(I)–(−)-DIOP-complex prepared *in situ* and Ru_2Cl_4((−)-DIOP)$_3$ with or without Et_3N. This is attributable to the favorable coordination of the substrate to the first-row transition metal complex as compared with the Rh(I) or Ru(II) complex.

From Table 2, it is obvious that the enantioselectivity of the Co(II)–(−)-DIOP complex is affected by the bulkiness of the ester moiety in the substrate. The bulky substituent decreased the hydrogenation ability of the catalytic system of $CoCl_2$–(−)-DIOP and Et_3N ($CoCl_2/Et_3N$ = ½), but the order of the enantioselectivity was not in accordance with that of the bulkiness of the ester moiety. The small methyl substituent brought about the change of the prevailing

TABLE 2

Asymmetric Hydrogenation of α-Methylcrotonates by *in Situ* Prepared Co(II)–(−)-DIOP Complex at 80°C in the Presence of Triethylamine[a]

(MeCH=C(Me)CO_2R) R	Time (h)	Yield (%)	e.e.[b] (%)
Me	22	21	4.5(*S*)
Et	22	17	11.7(*R*)
Bu^n	22	6	6.3(*R*)
l-Menthyl	36	5	11.4(*R*)

[a] [$CoCl_2$] = [(−)-DIOP] = 0.16 mmol and [Et_3N] = 0.32 mmol.

[b] Configuration in parentheses.

enantiomer in the product from (*R*)-isomer to (*S*)-one, and *l*-menthyl substituent clearly exhibited its chirality effect for the asymmetric induction of the $CoCl_2$(−)-DIOP–Et_3N system, even in the uneasy complexation between the catalytic system and the bulky substrate.

At any rate, the asymmetric inductive ability of Co(II) or Ni(II) chiral diphosphine complex was relatively higher in the hydrogenation of a small substrate than the Rh(I) or Ru(II) chiral diphosphine complex. Further study on the catalytic property and improvement of the catalytic efficiency of the present complexes is now in progress.

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Received June 2, 1983