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Rhodium(I) and platinum(II) complexes of aminomethylphosphines as hydrogenation and hydroformylation catalysts

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Hydrogenation of α-acetamidocinnamic acid with chiral aminomethylphosphine complexes of rhodium(I), [Rh(cyclo-octa-1,5-diene){$(R_2PCH_2)_2NR^1$}]PF_6 (R = Ph or Cy, R^1 = D(+)-CHMePh, L-$CHMeCO_2Et$, (*R*)(+)-bornyl) shows no asymmetric induction. The hydroformylation of styrene using the catalyst mixture $[PtCl_2(P-P)]/SnCl_2$ shows asymmetric induction with up to 31% enantiomeric excess of 2-phenylpropanol being observed.

Keywords: Hydrogenation, hydroformylation, rhodium(I), platinum(II), aminoalkylphosphines, catalyst

INTRODUCTION

The importance of tertiary phosphine complexes in homogeneous catalysis has prompted many fundamental studies of phosphine ligands.[1,2] Investigation of electronic and steric effects on the structure, bonding and catalytic effects have been facilitated by the ease with which phosphine substituents can be varied.[1–3] By comparison, aminomethylphosphines have received significantly less systematic study. We have begun a wide-ranging study of aminomethyl phosphines of the type $(R_2PCH_2)_2NR'$, which we have shown can be readily obtained by the reactions of primary amines with phosphonium salts of the type $[R_2P(CH_2OH)_2]Cl$ (R = Ph or Cy).[4] In particular, the ready availability of optically active amines provides a very convenient source of chiral phosphine ligands. Herein we describe some initial studies on the use of rhodium(I) and platinum(II) aminomethylphosphine complexes in asymmetric catalytic hydrogenation and hydroformylation.

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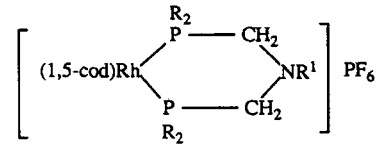
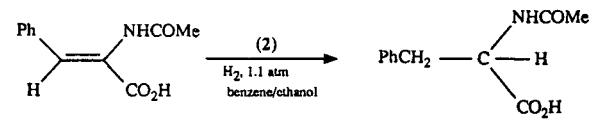
RESULTS AND DISCUSSION

The hydrogenation of (*Z*)-α-acetamidocinnamic acid (**1**) is a useful reaction for assessing asymmetric induction in homogeneous catalysis using rhodium(I) chiral phosphine catalysts.[5–7] In the present work, hydrogenation reactions were carried out using the cationic cyclo-octa-1,5-diene complexes (**4**) as catalysts. The details of the reaction



4a R=Ph, R^1=CHMePh
4b R=Ph, R^1=$CHMeCO_2Et$
4c R=Ph, R^1=(*R*)-(+)-bornyl
4d R=Cy, R^1=CHMePh
4e R=Cy, R^1=$CHMeCO_2Et$

are given in the Experimental section. The reaction is outlined in Scheme 1 and the substrate and conditions were selected to give direct comparison with previous work. The reaction times and overall and optical yields are given in Table 1. Results for the catalytic hydrogenation of **1** using $[RhCl(C_7H_8)]_2$ (C_7H_8 = norbornadiene) + $4PPh_3$ to give racemic products are presented as a general comparison. The reaction times were reasonably consistent at 5–6 h and were comparable with previous studies. The uptake of hydrogen was usually rapid at the beginning of a reaction but after 10–15 min it settled down to a steady rate, until the reaction was complete. The solvent ratio of benzene/ethanol of 1 : 1 has been reported



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Scheme 1

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Table 1 Catalytic hydrogenation of α-acetamidocinnamic acid

Catalyst precursor	Reaction time (h)	Chemical yield (%)	Optical yield[a] (%)
4a	6.15	79	0
4b	5.15	72	1.0
4c	5.00	85	2.0
4d	6.00	71	1.9
4e	6.00	80.5	2.4
$[Rh(NBD)Cl]_2 + 4\ PPh_3$	5.00	95	—

to give optimum rates of reaction[8] and was used in all experiments. The yields in all the hydrogenations were observed to be quantitative by ^1H NMR spectroscopy of the crude reaction mixtures. The presence of multiplets at δ 4.75 ppm (CH) and δ 3.1 ppm (—CH_2) are indicative of *N*-acetylphenylalanine (**3**) and integrated to exactly 1H and 2H respectively in relation to other signals. Also observed was the change of the phenyl region signals from overlapping multiplets at δ 7.2–7.7 ppm to a clearly defined single peak at δ 7.2 ppm. The enantiomeric excess of the products was measured by optical rotation against pure *N*-acetyl-L-phenylalanine, $[\alpha]_D^{22} + 47.4°$ (EtOH).

Optical yields reported for previous studies of structurally similar rhodium–aminomethylphosphine catalysts[6,8] (27–32% enantiomeric excess) could not be obtained in this study. From Table 1 it can be seen that the products from all the hydrogenations were essentially racemic, with all results being similar. It is clear that change in chiral substituents at nitrogen had no effect on reaction times, yields or optical yields. It was also observed that the presence of bulky cyclohexyl groups on the phosphine ligands had no noticeable effect on the reaction.

Table 2 Catalytic hydroformylation of styrene

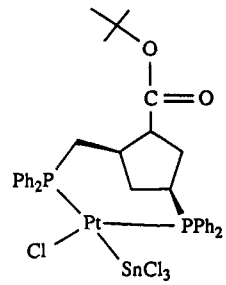
Catalyst precursor + $SnCl_2$	Chemical yield (%)	Product isomer ratio branch/chain	Optical yield (%)
6a	9	36:1	31
6b	No reaction	—	—
6c	15	7:1	23
6d	No reaction	—	—
6e	No reaction	—	—

Solvent: benzene. Reaction time: 6 h. Temperature: 60 °C. Pressure CO^+H_2: 100 atm (101×10^2 kPa). Pt/Sn ratio, 1:3. Pt/substrate ratio, 1:5000 approx.

Since it has been shown[9] that the hydroformylation of styrene with a complex of platinum(II) (**5**, Scheme 2) containing a chiral phosphine ligand in the presence of tin(II) chloride catalyses the hydroformylation of prochiral alkenes, it was also decided to investigate the activity of platinum(II) complexes containing aminoalkylphosphines.

Hydroformylation experiments were carried out under standard conditions for all the catalyst precursors, enabling the merits of each catalyst to be directly compared. The substrate styrene was selected as it has been a well-studied prochiral substrate in asymmetric catalytic hydroformylation with platinum–tin catalysts.[10–12] Previous studies[10–12] of this system have employed synthesis gas pressures of up to 180 atm (182×10^2 kPa). The results given in the present work were limited to the autoclave's maximum working pressure of 100 atm (101×10^2 kPa) but, as reaction rate is proportional to the overall pressure in these reactions[13] the results are relative. Initial studies showed that the percentage conversion and optical yields were identical for either preformed [PtCl ($SnCl_3$) (P—P)] catalysts or mixtures of the complexes **6** and tin(II) choride ($SnCl_2$). These latter catalysts were prepared *in situ* by dissolving the platinum complexes **6** in benzene and stirring with a three-fold excess of $SnCl_2$ for 20 min prior to adding the solution to the autoclave. The catalytic hydroformylation of styrene is outlined in Scheme 2. A summary of the results for the catalytic hydroformylation of styrene is given in Table 2 with a résumé of the reaction conditions.

Experiments involving cyclohexyl-substituted phosphines and/or ethyl-ester-substituted phosphines (**6b**, **6d**, **6e**) showed no reaction. Involvement of the ethyl ester group in the course of the reaction is unknown. Previous work[14] with chelating cyclohexylphosphines in similar hydroformylation catalysis have shown poor reactivity which has been attributed to electronic effects. However, the steric bulk of the cyclohexyl groups may also play a part in limiting the catalyst's activity, particularly in intermediates involved in the rate-limiting step. The catalyst system **6a** + $SnCl_2$ shows a large preference for the chiral branched product and gives the best results for asymmetric induction (31% e.e.). The catalyst system **6c** + $SnCl_2$ gives a slightly higher yield than **6a** but a lower branch/chain product ratio and a lower optical yield (23% e.e.). Most of the previous reports[11,12] of asymmetric hydroformylation of styrene using platinum–tin catalysts have shown typical branch/linear-chain product ratios



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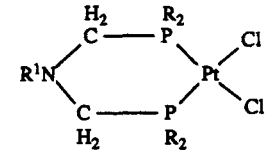

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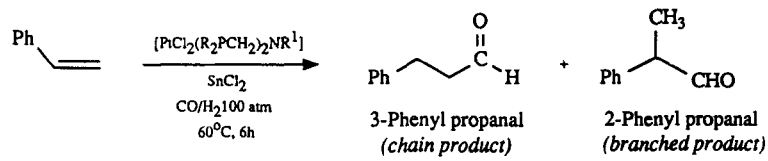

Scheme 2

of around 1.0–3.4. This demonstrates a very good selectivity for the chiral branched product by the **6a** + $SnCl_2$ system. The determination of optical yields in the hydroformylation of styrene was carried out by ^1H NMR spectroscopy and the chiral shift reagent tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium-(III), $[Eu(hfc)_3]$.[11]

CONCLUSION

Hydrogenation of α-acetamidocinnamic acid (**1**) with chiral aminomethylphosphine complexes of rhodium showed no asymmetric induction. Reaction rates and yields obtained from these catalysts show no advantage over existing complexes. The hydroformylation of styrene using chiral aminomethylphosphine complexes of platinum in the presence of $SnCl_2$ has shown asymmetric induction with up to 31% enantiomeric excess of 2-phenylpropanol being observed.

EXPERIMENTAL

Hydrogenations were carried out in a Schlenk flask fitted with a septum cap, connected to a standard hydrogenation apparatus. This consisted of a burette and bulb for monitoring gas uptake, a barometer, a hydrogen gas inlet and a vacuum pump outlet. Hydroformylations were carried out in a 100-cm^3 glass lined Roth autoclave, fitted with a thermostatted heating jacket and pressure head connected to a cylinder of synthesis gas (CO/H_2, 1:1). Optical rotations were measured with a Perkin–Elmer 141 polarimeter at a concentration of 5×10^{-3} g cm^{-3} in 95% ethanol. Styrene was obtained from commercial sources and distilled prior to use. The solvents ethanol and benzene were dried and distilled under a nitrogen atmosphere prior to use.

(*Z*)-α-Acetamidocinnamic acid and $Eu(hfc)_3$ were used as supplied from Aldrich. The catalyst precursors **4** and **6** were prepared from the appropriate ligand and either $[RhCl(cod)]_2$ or $[PtCl_2(cod)]$. Dihydrogen and synthesis gas (CO/H_2, 1:1) were used as supplied from commercial sources (BOC).

Hydrogenation of α-acetamidocinnamic acid using $[Rh(cod)(R_2PCH_2)_2NR']^+PF_6^-$ catalyst precursors

Hydrogenation reactions were carried out by identical methods for the catalyst precursors **4**.[13,14] The general procedure being as follows. The catalyst precursor (**4**) (0.01 g) was dissolved in a benzene–ethanol solution (1:1, 10 cm^3) and placed in a Schlenk flask fitted with a septum cap, under a nitrogen atmosphere. The substrate α-acetamidocinnamic acid (0.5 g, 2.4 mmol) was

also dissolved in a benzene–ethanol solution (1:1, 40 cm^3) under a nitrogen atmosphere. The Schlenk flask containing the catalyst solution was then connected to the hydrogenation apparatus and evacuated and purged with hydrogen, and the process was repeated. After the catalyst solution had been stirred under an atmosphere of hydrogen for 20 min the substrate solution was added via a syringe through the septum cap. The bulb of the hydrogenation apparatus was then adjusted to bring the internal pressure to 1.1 atm (111 kPa). This pressure was kept constant throughout the reaction time. The reaction was stopped when no further uptake of hydrogen was monitored on the burette, by evacuating the gas from the system. The reaction mixture was reduced to a residue under lowered pressure and the crude products were analysed by ^1H NMR in a solution of deuterochloroform. The residue was then dissolved in hot acetone and filtered through celite. The product, *N*-acetylphenylalanine, was crystallized out at −30 °C in a freezer. The product was then filtered and washed with cold dichloromethane to remove any remaining traces of catalyst. Optical rotation measurements were carried out on the products in ethanol solution using a pure sample of *N*-acetyl-L-phenylalanine, $[\alpha]_D^{22} + 47.4°$ (EtOH), as the reference.

Hydroformylation of styrene using the catalyst system $[PtCl_2(R_2PCH_2)_2NR'] + SnCl_2$

Hydroformylations were carried out by a standard procedure for the catalyst precursors **6**[13,14] using a standard time, temperature and pressure for all reactions (6 h, 60 °C, 100 atm/101×10^2 kPa). The general procedure was as follows. The catalyst precursor **6** (0.02 g, 0.25 mmol) and anhydrous $SnCl_2$ (0.02 g, 0.1 mmol) was dissolved in benzene (5 cm^3). The autoclave was purged with nitrogen and the catalyst solution and styrene (10 cm^3, 86.6 mmol) were then added. The autoclave was then flushed twice with synthesis gas (50 atm/50.6×10^2 kPa) and the pressure released. The vessel was then filled with synthesis gas (100 atm/101×10^2 kPa) and brought to a constant 60 °C for 6 h. After the reaction mixture had been allowed to cool, the pressure was slowly released and the mixture was distilled to separate it from the catalyst. The percentage conversion and the ratio of branch to chain products were determined by integration using ^1H NMR.

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