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PREPARATION AND CATALYTIC PROPERTIES OF CATIONIC RHODIUM(I) COMPLEXES CONTAINING 2,2′-BIS(DIPHENYLPHOSPHINO)BIPHENYL *

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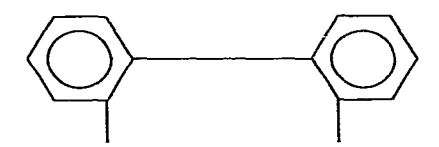
Summary

Complexes of the type [Rh(cod)(bpbp)]X (cod is 1,5-cyclooctadiene, bpbp is 2,2′-bis(diphenylphosphino)biphenyl, and X is Cl^-, *d*-α-bromocamphor-π-sulfonate [(*d*)-$C_{10}H_{14}O_4SBr]^-$, PF_6^- or $B(C_6H_5)_4^-$) are discussed, [Rh(cod)-(bpbp)][(*d*)-$C_{10}H_{14}O_4SBr$] was obtained in optically active form. The catalytic activities of these complexes were evaluated through the hydrogenation of 2-acetamidoacrylic acid (AAA) and α-acetamidocinnamic acid (ACA). They are so active that in their presence hydrogenation takes place at ambient temperatures and pressures. Hydrogenations by the use of the $(+)_{589}$-forms gave optically active *N*-acetyl-(*R*)-alanine and *N*-acetyl-(*R*)-phenylalanine.

Introduction

Many studies have been devoted to the selective hydrogenation of unsaturated organic compounds using homogeneous Pt^{II}, Pd^{II} and Ni^{II} catalysts [1]. Asymmetric hydrogenation is a matter of interest because it is a promising method for preparing optically active compounds. Several studies have shown that cationic metal complexes containing phosphines such as chiral P-atom



2,2′-Bis(diphenylphosphino) biphenyl

phosphines [2], chiral C-atom bisphosphines [3] and chiral P-atom bisphosphines [4] are efficient for the asymmetric hydrogenation of C=O, N=C and C=C

* Dedicated to Prof. R.C. Mehrotra on the occasion of his 60th birthday (February 16th, 1982).

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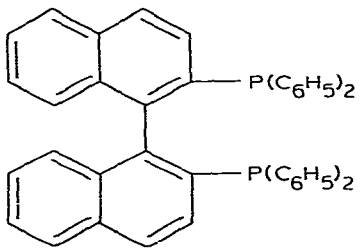
double bonds. In this study, we have used homogeneous Rh^I catalysts to effect asymmetric hydrogenation.

2,2′-Bis(diphenylphosphino)biphenyl (bpbp) has, in itself, no asymmetry, but its metal complexes are asymmetric because of the non-coplanarity of the two phenyl rings [5].

While this work was in progress, Takaya and his colleagues reported the preparation of rhodium complexes containing the analogous naphthyl compound [6].



This ligand is asymmetric even when not coordinated because of steric hindrance between the bulky naphthyl groups; when the rhodium(I) complex is used as a hydrogenation catalyst asymmetric products are obtained.

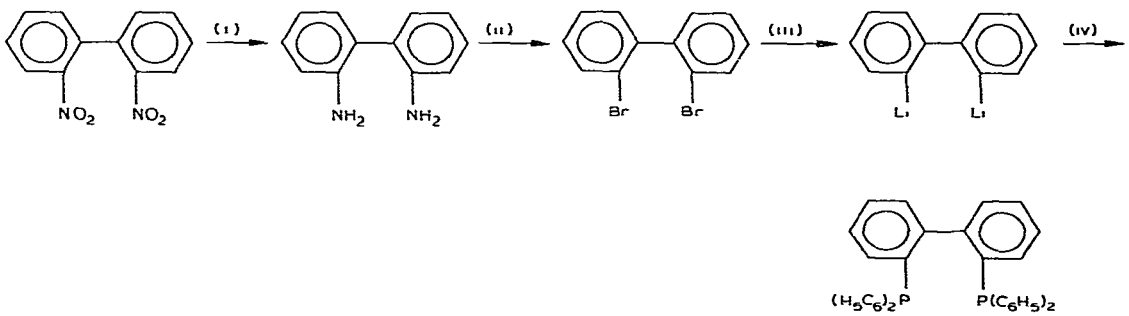
Experimental

Chemicals

The starting chemicals were 2-acetamidoacrylic acid (Aldrich Chemical Co.) and α-acetamidocinnamic acid (ICN Pharmaceuticals, Inc.). The reference chemicals, *N*-acetyl-(*R*)-alanine (Pfaltz and Bauer, Inc.) and *N*-acetyl-(*R*)-phenylalanine (Aldrich Chemical Co.), were purified from ethanol and their melting points were checked before use.

Preparation of 2,2′-bis(diphenylphosphino)biphenyl

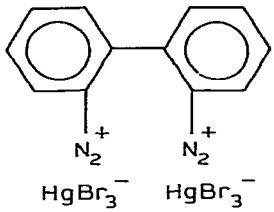
The preparative route for this compound is outlined below:



(i) 2,2′-Diaminobiphenyl was prepared by the reduction of 2,2′-dinitrobiphenyl [7]. m.p.: 78—79°C (lit. 78—79°C [7]).

(ii) 2,2′-Dibromobiphenyl was prepared by a modification of the published method [8]. A solution of 2,2′-diaminobiphenyl (3.6 g, 20 mmol) in 300 ml of 50% sulfuric acid was cooled to 0°C and a solution of sodium nitrite (2.8 g,

40 mmol) in 50 ml of water was added to it over 2—3 h with the temperature below 5°C. To the solution, a solution of mercury(II) nitrate (26 g, 80 mmol) and KBr (84 g, 700 mmol) in 35 ml of water was added rapidly. The yellow



product formed immediately. After 1 or 2 h, it was filtered in the dark, washed with cold water (2 × 50 ml) and cold acetone (2 × 30 ml) and allowed to dry. The product (20.5 g) was mixed with 41 g of KBr [9] and stored in the dark.

The mixture was spread thinly in a pyrex tube 60 cm × 2.5 cm of which one end was open and fitted with an air condenser. The tube was heated gently from the open end toward the closed end so that the tetrazonium salt was converted into dibromobiphenyl, which condensed along with the $HgBr_2$ in the cool part of the tube. The dibromobiphenyl was extracted with ether (2 × 50 ml). The ether was distilled off, leaving the faintly yellow dibromobiphenyl (5 g, 86%). This was recrystallized from 95% ethanol. m.p.: 80—81°C (lit. 80—81°C [7]).

(iii) 2,2′-Dilithiobiphenyl was prepared by a modification of the literature method [10,11]. Under a nitrogen atmosphere, 8.0 ml of a 1.8 *M* hexane solution of n-butyllithium [12] was added dropwise with stirring to a solution of 2,2′-dibromobiphenyl (2 g, 6.4 mmol) in anhydrous ether (25 ml) at 0°C. The reaction mixture was allowed to stand at room temperature for 4 h.

(iv) 2,2′-Bis(diphenylphosphino)biphenyl: To the above solution, a solution of chlorodiphenylphosphine (2.3 ml, 2.82 g, 1.25 mmol) in 10 ml of anhydrous ether was added dropwise over 30 min. The mixture was refluxed for 1 h, cooled to room temperature and then treated with cold, air-free water (25 ml) to destroy any remaining butyllithium. The ethereal layer was separated and dried with anhydrous Na_2SO_4, then evaporated to give crude, oily 2,2′-bis-(diphenylphosphino)biphenyl. Thin-layer chromatography revealed that the crude compound contained some impurity (probably phosphine monoxide). It was purified by means of silica-gel chromatography using toluene as the eluent [13]. The fractions containing the desired compound were combined, and the toluene was evaporated. The colorless, oily product was dissolved in 20 ml of ethanol; about 10 ml of water was added dropwise to precipitate the phosphine. The resulting solution was allowed to stand in a refrigerator overnight. 2.2 g (65%) of pure 2,2′-bis(diphenylphosphino)biphenyl was obtained (m.p. 68—70°C).

Found: C, 82.60; H, 5.55; P, 12.01. Calcd. for $C_{36}H_{28}P_2$: C, 82.74; H, 5.40; P, 11.85%.

Preparation of complexes

Di-μ-chlorobis(1,5-cyclooctadiene)dirhodium(I) ($[Rh(cod)Cl]_2$) was pre-

pared by the method of Chatt and Venanzi [14], and recrystallized from hot glacial acetic acid.

1,5-Cyclooctadiene-2,2'-bis(diphenylphosphino)biphenylrhodium(I) chloride, [Rh(cod)(bpbp)]Cl

522 mg (1 mmol) of bpbp was dissolved in 10 ml of acetone and 247 mg (0.5 mmol) of $[Rh(cod)Cl]_2$ was added with stirring. The mixture was evaporated to dryness. The product was purified by dissolving it in 5 ml of acetone and precipitating it by adding 5 ml of ether. Yield 220 mg (28%).

Found: C, 68.69; H, 5.14; P, 8.37; Cl, 4.75. Calcd. for $C_{44}H_{40}P_2ClRh$: C, 68.71; H, 5.24; P, 8.05; Cl, 4.61%.

Optical resolution of [Rh(cod)(bpbp)]$^+$

493 mg (1 mmol) of $[Rh(cod)Cl]_2$ and 1044 mg (2 mmol) of bpbp were dissolved in 10 ml of acetone. At this point, the orange-yellow compound ([Rh(cod)(bpbp)]Cl) was often precipitated. In either case, 836 mg (2 mmol) of solid silver *d*-α-bromocamphor-π-sulfonate was added. The resulting solution was stirred for about 3 h. The AgCl was filtered off, and the filtrate was evaporated almost to dryness. The product was collected and dried under vacuum. Yield, 1.98 g (94%).

Found: C, 61.59; H, 5.24; P, 5.69; S, 2.85; Br, 7.44. Calcd. for $C_{54}H_{54}O_4SBrRh$: C, 62.13; H, 5.21; P, 5.93; S, 3.08; Br, 7.65%.

The compound is extremely soluble in acetone, dichloromethane, ethanol and methanol, moderately soluble in ether, and insoluble in water.

TABLE 1

ROTATION DATA FOR FRACTIONS OF [Rh(cod)(bpbp)] [(*d*)-$C_{10}H_{14}O_4SBr$]

Fraction	Wt. of fraction (mg)	Sample amount [a] (mg)	Rotations obsd. (deg)		$[\alpha]_D^{25}$ [b]
F-1 [c]	340	6.0	0.065 0.062 0.064 0.062	0.063	21.2
F-2	120	5.0	0.042 0.041 0.043 0.045	0.043	17.4
F-3	250	4.2	0.067 0.063 0.068 0.063	0.065	30.8
F-4 [d]	260	4.6	0.071 0.075 0.073 0.074	0.073	34.5

[a] 2 ml of acetone was used as the solvent. [b] 22.1° was the rotation of 10 mg of Ag(*d*)-$C_{10}H_{14}O_4SBr$ in 10 ml of acetone, which contains almost the same amount of sulfonate ion as that in the complexes. [c] Undissolved fraction. [d] To dryness.

970 mg (0.9 mmol) of [Rh(cod)(bpbp)][(*d*)-$C_{10}H_{14}O_4SBr$] was partially dissolved in 500 ml of ether. The undissolved material was collected by filtration (fraction 1; F-1). The filtrate was allowed to stand in a vacuum desiccator at room temperature to get fractions 2, 3 and 4. Table 1 gives the rotation of each fraction. A solution of Ag(*d*)-$C_{10}H_{14}O_4SBr$ containing almost the same amount of sulfonate showed $[\alpha]_D^{25} = +22.1°$. Thus, the results in Table 1 imply that F-1 is not resolved; F-2 is somewhat enriched in the *l*-form; and F-3 and F-4 are rich in the *d*-form. The fact that F-3 and F-4 had about the same rotation indicates that they are almost optically pure. They were combined and fractions were treated with NH_4PF_6, $NaB(C_6H_5)_4$, or concentrated HCl to convert the bromo-camphorsulfonate to salts of these anions.

Conversion of the sulfonate into the hexafluorophosphate

100 mg (0.6 mmol) of NH_4PF_6 was added to a solution of 180 mg (0.17 mmol) of [Rh(cod)(bpbp)][(*d*)-$C_{10}H_{14}O_4SBr$] in 5 ml of ethanol. 1 ml of water was added drop by drop to precipitate [Rh(cod)(bpbp)]PF_6. The precipitate was collected and dried over P_2O_5. Yield, 95 mg (64%). $[\alpha]_D^{25} = 6.3°$ (in acetone).

Found: C, 59.62; H, 4.75; P, 10.32. Calcd. for $C_{44}H_{40}P_3F_6Rh$: C, 60.15; H, 4.59; P, 10.57%.

Fraction F-2 (120 mg, 0.12 mmol) was treated similarly to give (—)[Rh(cod)-(bpbp)]PF_6 (58 mg, 62%). The compound showed $[\alpha]_D^{25} = -0.8°$, which is too small to give useful results.

Conversion of the sulfonate into the tetraphenylborate

220 mg (0.21 mmol) of [Rh(cod)(bpbp)][(*d*)-$C_{10}H_{14}O_4SBr$] was dissolved in 10 ml of methanol, and 80 mg (0.23 mmol) of solid $NaB(C_6H_5)_4$ was gradually added with stirring. The yellow precipitate was dried over P_2O_5. Yield, 98 mg (43%). $[\alpha]_D^{25} = 6.5°$ (in acetone).

Found: C, 76.81; H, 5.49; P, 5.73. Calcd. for $C_{68}H_{60}P_2BRh$: C, 77.57; H, 5.74; P, 5.88%.

Conversion of the sulfonate into the chloride

A solution of 250 mg (0.24 mmol) of [Rh(cod)(bpbp)][(*d*)-$C_{10}H_{14}O_4SBr$] in 10 ml of methanol was cooled in an ice-salt bath, and concentrated hydrochloric acid was added dropwise until a yellow precipitate appeared. The resulting mixture was allowed to stand in the ice-salt bath overnight. The yellow product was collected by filtration and dried over P_2O_5. Yield, 73 mg (39%). $[\alpha]_D^{25} = 5.8°$ (in acetone).

Found: C, 68.56; H, 5.21; P, 8.11; Cl, 4.64. Calcd. for $C_{44}H_{40}P_2ClRh$: C, 68.71; H, 5.24; P, 8.05; Cl, 4.61%.

Apparatus

Infrared absorption spectra were measured in Nujol mull using a Perkin-Elmer 599B infrared spectrophotometer. Proton magnetic resonance spectra were monitored on a Varian EM-390 instrument at 34°C in dimethyl-d_6 sulfoxide with TMS as the internal reference. Optical rotations were measured in a 1 dm cell with a Rudolph Research automatic polarimeter model III at ambient temperatures and the values observed were corrected to those at 25°C.

Hydrogenation experiments

A bench-size 300 ml stainless steel Magne-Drive autoclave was used for the hydrogenation experiments at pressures higher than 1 atm. The hydrogenation runs at ambient pressures were carried out in a 100 ml 2-neck round-bottom flask. 2-Acetamidoacrylic acid (AAA) (3—4 mmol) or α-acetamidocinnamic acid (ACA) (2—3 mmol) was dissolved in 25—30 ml of 99.8% CH_3OH, to which a solution of each catalyst (0.05—0.1 mmol) in 5 ml of acetone was added.

After hydrogenation, the resulting solutions were evaporated to dryness: In the case of 2-acetamidoacrylic acid, the hydrogenated acid was dissolved in 10 ml of water and separated from the catalyst by filtration. Evaporation of the filtrate afforded the product. In the case of α-acetamidocinnamic acid, the organic residue was dissolved in 0.5 *M* aqueous sodium hydroxide. The solution was filtered to remove the catalyst, acidified with dilute hydrochloric acid and extracted with ether. The ethereal phase was washed with a little water, dried over anhydrous sodium sulfate and evaporated to dryness. The products thus obtained were identified from their melting points, analytical data, IR spectra and NMR spectra.

Results and discussion

Identification of the product

Table 2 contains melting points and diagnostic IR data for the starting substrates, and the racemic and optically active products. Inspection of the table reveals that the comparison of melting points and IR data tells not only whether

(Continued on p. 9)

TABLE 2

MELTING POINTS AND DIAGNOSTIC IR DATA

(A) 2-Acetamidoacrylic acid, and racemic and optically active N-acetylalanine

	2-Acetamidoacrylic acid	Racemic *N*-acetylalanine	*N*-Acetyl-(*R*)-alanine
m.p. (°C)	185—186	135—138	110—115
IR data (cm^{-1}) [a]			
ν(N—H)	3360vs	3360vs	3320vs
ν(C=O)	1720vs	1725vs	1705vs
$\nu(C{=}O)_2$	1645, 1620vs	1595vs	1615vs
δ(N—H)	1545vs	1550vs	1555vs

(B) α-Acetamidocinnamic acid, and racemic and optically active N-acetylphenylalanine

	α-Acetamidocinnamic acid	Racemic *N*-Acetyl-phenylalanine	*N*-Acetyl-(*R*)-phenylalanine
m.p. (°C)	194—195	143—145	170—171
IR data (cm^{-1})			
ν(N—H)	3250vs,br	3390vs	3339vs
ν(C=O)	1690vs	1705vs	1700vs
$\nu(C{=}O)_2$	1653vs	1620vs,br	1620vs
δ(N—H)	1510s	1565vs	1555vs,br

[a] ν(N—H): N—H stretching vibration; ν(C=O): C=O stretching vibration; $\nu(C{=}O)_2$: $(C{=}O)_2$ stretching vibration; δ(N—H): N—H bending vibration. vs: very strong; vs,br very strong and broad; s: strong.

TABLE 3

CATALYTIC HYDROGENATION OF 2-ACETAMIDOACRYLIC ACID

Exp.	Hydrogenation conditions			Products		
	Catalysts	Hydrogen press. (p.s.i.)	time (min)	Chemical yield [a] (%)	$[\alpha]_D^{25}$ (°)	Optical yield [b] (%)
1	$[Rh(cod)Cl]_2$ + 2bpbp [c]	200	120	95	0	0
2	$[Rh(cod)Cl]_2$ + 4bpbp [c,d]	200	120	38	0	0
3	$[Rh(cod)Cl]_2$ + 2bpbp [c]	Atm.	300	95	0	0
4	$[Rh(cod)Cl]_2$ + 4bpbp [c]	Atm.	300	~0	—	—
5	[Rd(cod)(bpbp)]Cl	Atm.	300	97	0	0
6	[Rh(cod)(bpbp)][(*d*)-$C_{10}H_{14}O_4SBr$]	Atm.	300	95	0	0
7	(+)-[Rh(cod)(bpbp)]PF_6 ($[\alpha]_D^{25}$: 6.5°)	Atm.	300	94	8.6	12.9
8	(+)-[Rh(cod)(bpbp)]Cl ($[\alpha]_D^{25}$: 5.8°)	Atm.	300	95	7.6	11.4
9	(+)-[Rh(cod)(bpbp)]$B(C_6H_5)_4$ ($[\alpha]_D^{25}$: 6.5°)	Atm.	300	85	5.7	8.6

[a] Chemical yield shows the yield of the product, and therefore indirectly reflects the extent of hydrogenation. [b] Optical yield was calculated with respect to the value for the optically pure compound: *N*-acetyl-(*R*)-alanine, $[\alpha]_D$ = 66.5° (2 g/100 H_2O) [15]. [c] These catalysts were prepared in situ. Acetone was used as the solvent. [d] Control experiments showed that 2-acetamidoacrylic acid is hydrogenated to the same degree at 200 psi for 120 min without a catalyst.

TABLE 4

CATALYTIC HYDROGENATION OF α-ACETAMIDOCINNAMIC ACID

Exp.	Hydrogenation conditions			Products		
	Catalysts	Hydrogen press. (p.s.i.)	time (min)	Chemical yield [a] (%)	$[\alpha]_D^{25}$ (°)	Optical yield [b] (%)
10	$[Rh(cod)Cl]_2$ + 2bpbp [c]	500	120	93	0	0
11	$[Rh(cod)Cl]_2$ + 4bpbp [c,d]	500	120	20	0	0
12	$[Rh(cod)Cl]_2$ + 2bpbp [c]	Atm.	360	92	0	0
13	$[Rh(cod)Cl]_2$ + 4bpbp [c]	Atm.	360	0	—	—
14	[Rh(cod)(bpbp)]Cl	Atm.	360	93	0	0
15	[Rh(cod)(bpbp)][(*d*)-$C_{10}H_{14}O_4SBr$]	Atm.	360	93	0	0
16	(+)-[Rh(cod)(bpbp)]PF_6 ($[\alpha]_D^{25}$: 6.5°)	Atm.	360	94	−3.4	6.5
17	(+)-[Rh(cod)(bpbp)]Cl ($[\alpha]_D^{25}$: 5.8°)	Atm.	360	93	−3.2	6.1
18	(+)-[Rh(cod)(bpbp)]$B(C_6H_5)_4$ ($[\alpha]_D^{25}$: 6.5°)	Atm.	360	82	−2.6	5.0

[a] Chemical yield shows the yield of the product, and therefore indirectly reflects the extent of hydrogenation. [b] Optical yield was calculated with respect to the value for the optically pure compound, *N*-acetyl-(*R*)-phenylalanine $[\alpha]_D$ = −51.8 (Cl, ethanol) [16]. [c] These catalysts were prepared in situ. Acetone was used as the solvent. [d] Control experiments showed that 2-acetamidoacrylic acid is hydrogenated to the same degree at 200 psi for 120 min without a catalyst.

the product is completely hydrogenated but also whether the product is racemic and/or optically active.

Effect of ratios of Rh^I to bpbp on hydrogenation

Catalysts of various ratios of Rh^I to bpbp were prepared in situ and their catalytic activities were examined at different hydrogen pressures. Typical results are exemplified by exps. 1—4 (Table 3) and exps. 10—13 (Table 4). When the ratio is 1:1, the chemical yields were in the order of 90% at high (exps. 1 and 10) and low pressures (exps. 3 and 12). On the other hand, when the ratio was 1:2, the chemical yields were almost zero (exps. 4 and 13) at low hydrogen pressures, and 38% (exp. 2) and 20% (exp. 11) at high pressures. These results indicate that (1) complexes in which the ratio of Rh to bpbp is 1 to 1 are active catalysts for the hydrogenation of AAA and ACA; (2) complexes in which the ratio is 1 to 2 have no effect on the hydrogenation because of the formation of $[Rh(bpbp)_2]^+$, in which 2 moles of bpbp are strongly coordinated to the rhodium and probably prevent the coordination of substrates; (3) AAA and ACA are hydrogenated even without catalysts at such high hydrogen pressures and (4) AAA is more easily hydrogenated than ACA. On the basis of these results, we then prepared the complexes of 1:1 Rh:bpbp ratio and their catalytic activities were examined at low hydrogen pressures.

Effect of anions on hydrogenation

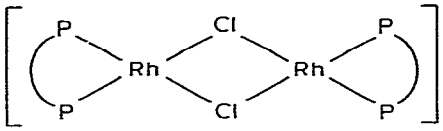
As seen from Tables 3 and 4, when the anion is Cl^-, $[(d)\text{-}C_{10}H_{14}O_4SBr]^-$ or PF_6^-, the chemical yields are in the order of 93—97% for AAA (exps. 5—8) and 92—94% for ACA (exps. 14—17); namely, the catalytic activities for hydrogenation were almost the same irrespective of the anion except for the case of the tetraphenylborate. When the anion is $B(C_6H_5)_4^-$, the chemical yields are only 85% for AAA (exp. 9) and 82% for ACA (exp. 18). This may be due to the coordination of $B(C_6H_5)_4^-$ to Rh^I through a $\pi(h^6)$-bonded interaction, which has been reported to greatly alter and impair the catalytic ability in homogeneous hydrogenation [17].

Effect of optically active complexes on asymmetric hydrogenation

Optical yields for the hydrogenation of AAA (exps. 7—9) and for that of ACA (exps. 16—18) were 8—13% and 5—6.6%, respectively. $[\alpha]_D^{25}$ in exps. 7—9 were only 5.7° to 8.6° and those in exps. 16—18 were —2.6° to —3.4°, which indicates that (+)-[Rh(cod)(bpbp)]PF_6, (+)-[Rh(cod)(bpbp)]Cl and (+)-[Rh(cod)(bpbp)]$B(C_6H_5)_4$ are moderately effective for asymmetrically converting AAA and ACA into *N*-acetyl-(*R*)-alanine and *N*-acetyl-(*R*)-phenylalanine, respectively.

Finally, it should be noted that the chloride can be used repeatedly in the hydrogenation of AAA. For example, the catalyst after work-up of exp. 8 was dissolved in about 5 ml of acetone, and the solution was used again for the hydrogenation of AAA. The chemical and optical yields were 95% and 10.8%, respectively. This indicates that the catalyst is not racemized during use. We have recently found that this is also true for the Rh^I complexes of bis(1,2-diphenylphosphino)ethane (diphos) and (—)-2,3-*o*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (diop) [18]. The reason why

only the chloride can be reused is still uncertain, but it seems that in the case of chloride, the structure of the complex may be preserved even during and after the work-up steps as the following dimer.



P——P : Bisphosphine

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References

1 See for example:
(a) H. Itatani and J.C. Bailar, Jr., Ind. Eng. Chem. Prod. Res. Develop., 11 (1972) 146; (b) H.B. Bruner and J.C. Bailar, Jr., J. Am. Oil Chem. Soc., 49 (1972) 533; (c) H.B. Bruner and J.C. Bailar, Jr., Inorg. Chem., 12 (1973) 1465; (d) J.C. Bailar, Jr., J. Indian Chem. Soc., 54 (1977) 1; (e) Y. Fujii and J.C. Bailar, Jr., J. Catalysis, 55 (1978) 146 and references therein.
2 (a) W.S. Knowles, M.J. Sabacky and B.D. Vineyard, J. Chem. Soc. Chem. Commun., (1972) 10; (b) P. Bonvincini, A. Levi, G. Modena and G. Scorrano, J. Chem. Soc. Chem. Commun., (1972) 1188; (c) K. Yamamoto, T. Hayashi and M. Kumada, J. Organometal. Chem., 54 (1973) C45; (d) M. Tanaka, Y. Watanabe, T. Mitsudo, H. Iwane and Y. Takegami, Chem. Lett., (1973) 239.
3 (a) T.P. Dang, J.C. Poulin and H.B. Kagan, J. Organometal. Chem., 91 (1975) 105; (b) A. Levi, G. Modena and G. Scorrano, J. Chem. Soc. Chem. Commun., (1975) 6.
4 (a) W.S. Knowles, M.J. Sabacky, B.D. Vineyard and D.J. Weinkauff, J. Am. Chem. Soc., 97 (1975) 2567; (b) H.B. Kagan and T.P. Dang, J. Am. Chem. Soc., 94 (1972) 6429.
5 T. Habu and J.C. Bailar, Jr., J. Am. Chem. Soc., 88 (1966) 1128.
6 (a) K. Toriumi, T. Ito and H. Takaya, I.M.S. Ann. Rev., (1979) 118; (b) H. Takaya, A. Yasuda and M. Yamanaka, I.M.S. Ann. Rev., (1979) 136.
7 R.E. Moore and A. Furst, J. Org. Chem., 23 (1958) 1504.
8 H.W. Schwechten, Ber., 65B (1932) 1605.
9 KBr was used as the diluent.
10 D.W. Allen, I.T. Millan and F.G. Mann, J. Chem. Soc. (C), (1967) 1869.
11 S.A. Gardner, H.B. Gordon and M.D. Rausch, J. Organometal. Chem., 60 (1973) 179.
12 The concentration of the solution was determined by the method of S. Watson and J. Eastham, J. Organometal. Chem., 9 (1967) 165.
13 Column was 30 cm high and 3.5 cm in diameter.
14 J. Chatt and L.M. Venanzi, J. Chem. Soc., (1957) 4735.
15 S.M. Birnbaum, L. Levintow, R.B. Kingsley and J.P. Greenstein, J. Biol. Chem., 194 (1952) 455.
16 F. Knoop and J.G. Banco, Z. Phys. Chem., 146 (1925) 272.
17 R.R. Schrock and J.A. Osborn, Inorg. Chem., 9 (1979) 2339.
18 Under investigation.