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Asymmetric synthesis catalyzed by chiral ferrocenylphosphine–metal complexes

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Abstract - Optically active ferrocenylphosphines containing, on the side chain, hydroxy group appropriately distant from the ferrocene nucleus have been found to be effective ligands for the palladium-catalyzed asymmetric allylic alkylation of 1,3-disubstituted 2-propenyl acetates with sodium acetylacetonate and related soft carbon nucleophiles to give the alkylation products of up to 96% ee. A gold(I) complex of the chiral ferrocenylphosphines which have tertiary amines on the side chain have been found to catalyze the reaction of methyl isocyanoacetate with aldehydes in dichloromethane to give optically active trans-4-methoxycarbonyl-5-alkyl-2-oxazolines with high enantioselectivity (up to 98% ee) in a quantitative yield.

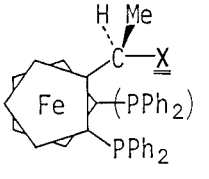
INTRODUCTION

In recent years, asymmetric carbon-carbon bond forming reactions catalyzed by transition-metal complexes containing optically active phosphine ligands have been the subjects of increased research activity (ref. 1). One of the most interesting and challenging problems in research on the catalytic asymmetric synthesis is development of the ligand which will fit in with a given reaction as efficiently in stereoselectivity as possible. Chiral ferrocenylphosphines have been demonstrated to be superior to others in that structural modification can be readily made by introduction of a desired functional group on the side chain according to the demand of the reaction type (ref. 2). They are effective for asymmetric hydrogenation of olefins (ref. 3) and ketones (ref. 4), asymmetric hydrosilylation of dienes (ref. 5), asymmetric cross-coupling forming olefins and allylsilanes (ref. 6 & 7), asymmetric allylation of active methine compounds (ref. 8). Here we describe some recent results of palladium(0)-catalyzed asymmetric allylic alkylation of substituted allyl acetates with carbon nucleophiles and gold(I)-catalyzed asymmetric aldol reaction of isocyanoacetate with aldehydes forming optically active oxazolines.

CHIRAL FERROCENYLPHOSPHINE LIGANDS

Optically active ferrocenylphosphines, which are readily prepared by way of stereoselective lithiation of optically resolved N,N-dimethyl-1-ferrocenylethylamine (ref. 9 & 10), have the unique and significant features shown in Scheme 1. Of these features, the most significant is the functional groups on the side chain. They are controlled by the ferrocenyl and methyl groups on the chiral carbon center to face to the reaction site on the catalyst coordinated with phosphorus atoms on the ferrocenylphosphine ligand and are expected to interact with a functional group on the substrate in a catalytic asymmetric reaction to bring about high stereoselectivity.

Scheme 1



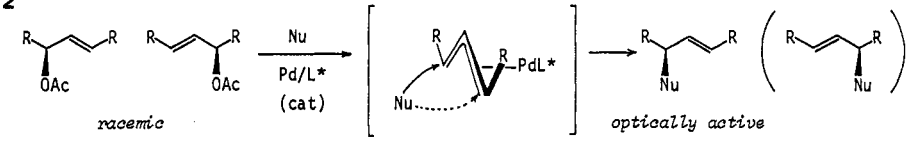
(*R*)-(*S*)-BPPF-X

1. Functional Groups on the Side Chain
2. Ferrocene Planar Chirality
3. Monophosphines and Bisphosphines
4. Stable in Air. Orange Color.

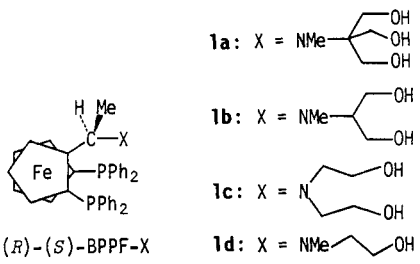
ASYMMETRIC ALLYLIC ALKYLATION

We have previously reported the asymmetric allylation of active methine compounds in the presence of chiral phosphine-palladium complexes which creates a new chiral carbon center in the nucleophiles (ref. 11). Here we describe another type of asymmetric allylation, that is, the reaction which creates a new chiral carbon center in allylic substrates (ref. 12). In the reaction of racemic 2-propenyl acetates which have the same substituent groups at 1 and 3 positions, the π-allylpalladium intermediate containing a meso type π-allyl group is formed from both enantiomers of the allylic substrate, and the asymmetric induction arises from preferential attack by a soft carbon nucleophile on either of the diastereotopic π-allyl carbon atoms in the intermediate (Scheme 2).

Scheme 2



Studies on stereochemistry of the allylic alkylation have revealed that soft carbon nucleophiles represented by sodium dimethyl malonate attack the π-allyl carbon from the side opposite to the palladium (ref. 13). On the basis of the mechanism, the functional groups which are expected to interact with the incoming nucleophile to bring about high stereoselectivity (Figure 1), were introduced at the side chain of chiral ferrocenylphosphines. Thus, the ferrocenylphosphines **1a, 1b, 1c,** and **1d** were prepared from (R)-1-[(S)-1',2-bis(diphenylphosphino)ferrocenyl]ethyl acetate (ref. 10).



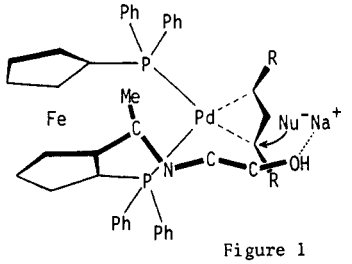
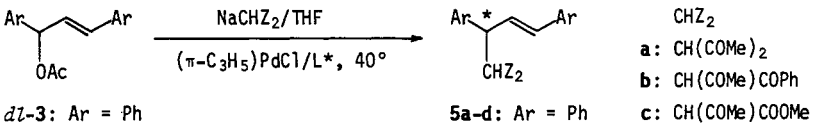


Figure 1

The ferrocenylphosphines were examined for stereoselectivity in the reaction of racemic (E)-1,3-diphenyl-3-acetoxy-1-propene (**3**) with sodium acetylacetonate in THF (Scheme 3). The reaction conditions and results are summarized in Table 1, which also contains data obtained with other phosphine ligands for comparison.

Scheme 3



dl-**3**: Ar = Ph
dl-**4**: Ar = 3-MeOC$_6$H$_4$

5a-d: Ar = Ph
6a: Ar = 3-MeOC$_6$H$_4$

The highest stereoselectivity was obtained in the reaction with the ferrocenylphosphine containing N-methyl-N-tris(hydroxymethyl)methylamino group (**1a**), which gave (S)-(E)-1,3-diphenyl-2-propenylacetylacetone (**5a**) of 96% ee in a high yield (entry 1). The ferrocenylphosphines **1b, 1c,** and **1d** which have 2-hydroxyethyl group(s) on the amino side chain were also effective in producing (S)-(E)-**5a** of over 70% ee (entries 2-5). The stereoselectivity achieved here is among the highest for the catalytic asymmetric carbon-carbon bond forming reactions (ref. 1). Lower selectivity was observed in the reaction with the ligands **2a**, **2b**, and **2c**, which are the ferrocenylphosphines lacking the hydroxy group (entries 6-8). It is probable that the hydroxy groups on the ligand **1a**, **1b**, 1c, or **1d** which are located outside the π-allyl of the π-allylpalladium intermediate, interact attractively with the acetylacetonate by hydrogen bonding as shown in Figure 1, and the interaction is responsible for the high stereoselectivity, controlling the attack of the nucleophile on the π-allyl carbon.

Introduction of the hydroxy group at the ferrocenylmethyl position in the ligand **2d** brought about the reversal of the stereocontrol to give (R)-**5a** of 46% ee (entry 9). The use of (-)-DIOP (ref. 14) or BPPM (ref. 15) resulted in the formation of almost racemic product **5a** (entries 10 and 11). The inefficiency of these ligands is ascribed to the lack of functional groups which can interact with the nucleophile. Sodium salts of benzoylacetone and methyl acetoacetate were also successfully used for the asymmetric alkylation of **3** to give the corresponding products **5b** and **5c** with (S) configuration of 87% and 83% ee, respectively (entries 12 and 13).

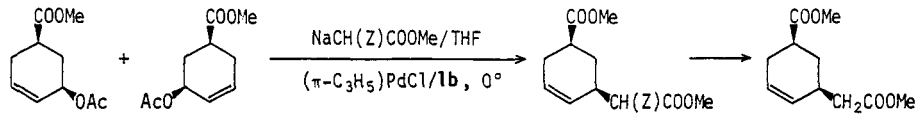
Table 1. Asymmetric Allylic Alkylation of (E)-1,3-Diphenyl-3-acetoxy-1-propene (**3**) Catalyzed by Chiral Ferrocenylphosphine-Palladium Complexes.[a]

entry	-X in (R)-(S)-BPPF-X	nucleophile	product	yield[b](%)	% ee	(confign)
1	$-NMeC(CH_2OH)_3$ (**1a**)	$NaCH(COMe)_2$	**5a**	85	96	(S)
2	$-NMeCH(CH_2OH)_2$ (**1b**)		**5a**	97	90	(S)
3[c]	$-NMeCH(CH_2OH)_2$ (**1b**)		**6a**	80	86	
4	$-N(CH_2CH_2OH)_2$ (**1c**)		**5a**	86	81	(S)
5	$-NMeCH_2CH_2OH$ (**1d**)		**5a**	86	71	(S)
6	$-NMe_2$ (BPPFA, **2a**)		**5a**	51	62	(S)
7	$-\overline{N-(CH_2)_5}$ (**2b**)		**5a**	90	44	(S)
8	-Me (**2c**)		**5a**	92	10	(R)
9	-OH (BPPFOH, **2d**)		**5a**	26	46	(R)
10	(-)-DIOP		**5a**	88	0	
11	BPPM		**5a**	86	7	(R)
12	$-NMeCH(CH_2OH)_2$ (**1b**)	NaCH(COMe)COPh	**5b**	93	87	(S)
13	$-NMeCH(CH_2OH)_2$ (**1b**)	NaCH(COMe)COOMe	**5c**	96	83	(S)

[a] To a mixture of a ligand (0.011 mmol), di-μ-chlorobis(π-allyl)dipalladium (0.005 mmol), and the acetate **3** (1.0 mmol) in THF (5 ml) was added a suspension of sodium enolate prepared from sodium hydride (1.2 mmol) and acetylacetone or a related active methylene compound (1.5 mmol) in THF (5 ml) at room temperature. The mixture was stirred at 40°C for 13-19 hr. After hydrolysis and the usual work-up, the product was isolated by preparative TLC on silica gel (hexane/ethyl acetate = 5/1). [b] Isolated yield. [c] Reaction of racemic (E)-1,3-di(3-methoxyphenyl)-3-acetoxy-1-propene (**4**).

The high efficiency of the palladium catalyst coordinated with the ferrocenylphosphine **1** was also observed in the reaction of cyclic acetate **7**, which gave the alkylation products (R,R)-**8a** and -**8b** of over 70% ee (Scheme 4).

Scheme 4



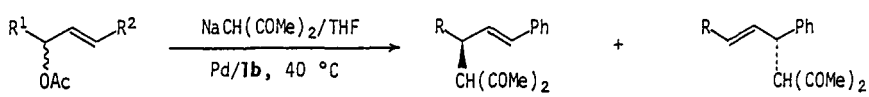
dl-**7**

Z = COMe: 97% (*R*,*R*)-**8a**, 71% ee (*S*,*S*)

Z = COOMe: 95% (*R*,*R*)-**8b**, 72% ee

The reaction of racemic 2-propenyl acetates substituted with two different aryl groups at 1 and 3 positions which should include chiral π-allylpalladium complex in the catalytic cycle was also carried out (ref. 16). Reaction of racemic (E)-1-(3-methoxyphenyl)-3-phenyl-3-acetoxy-1-propene (**9a**) with sodium acetylacetonate in THF at 40 °C for 45 h in the presence of 1 mol% of the palladium catalyst complexed with the chiral ferrocenylphosphine **1b** gave 92% yield of allylic alkylation products consisting of (S)-[(E)-styryl]-(3-methoxyphenyl)methyl-acetylacetone (**10a**) (95% ee) and its regioisomer (S)-**11a** (80% ee) in a ratio of 44/56 (Scheme 5). It should be noted that both of the regioisomeric alkylation products have (S) configuration and the enantiomeric purities of over 80% ee.

Scheme 5



9a: R^1 = Ph, R^2 = 3-$MeOC_6H_4$

9b: R^1 = 1-Np, R^2 = Ph

9c: R^1 = 4-ClC_6H_4, R^2 = Ph

9d: R^1 = 4-MeC_6H_4, R^2 = Ph

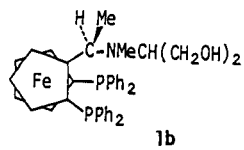
10a: R = 3-$MeOC_6H_4$

10b: R = 1-Np

10c: R = 4-ClC_6H_4

10d: R = 4-MeC_6H_4

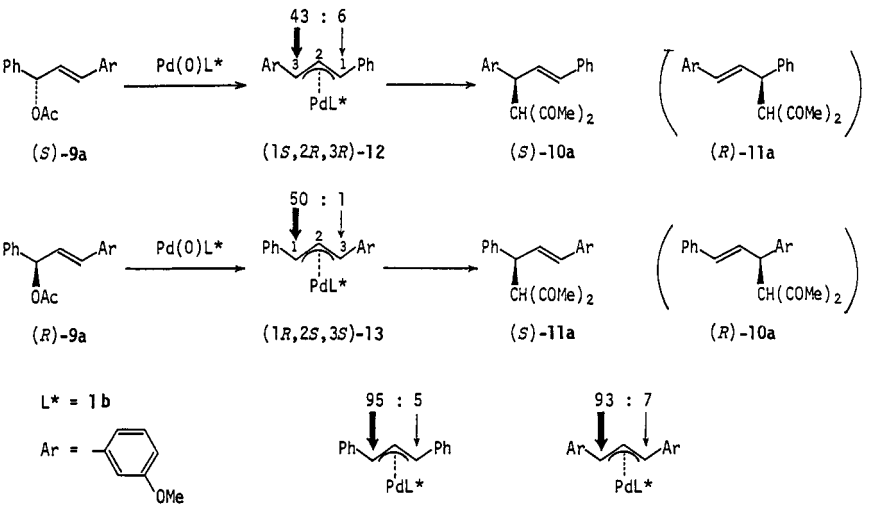
11a-d



1b

The stereochemical results can be visualized by Scheme 6. Oxidative addition of (S)-**9a** to a chiral phosphine-palladium(0) species with inversion of configuration at the allylic carbon (ref. 17) will form π-allylpalladium complex **12** which has (1S,2R,3R)-1-phenyl-3-(3-methoxyphenyl)-π-allyl group, and the diastereomeric π-allylpalladium complex **13**, which has the π-allyl group of opposite configuration (1R,2S,3S), will be formed from (R)-**9a**. The nucleophilic attack on C-1 carbon of π-allylpalladium complexes **12** and **13** will produce (R)-**11a** and

Scheme 6



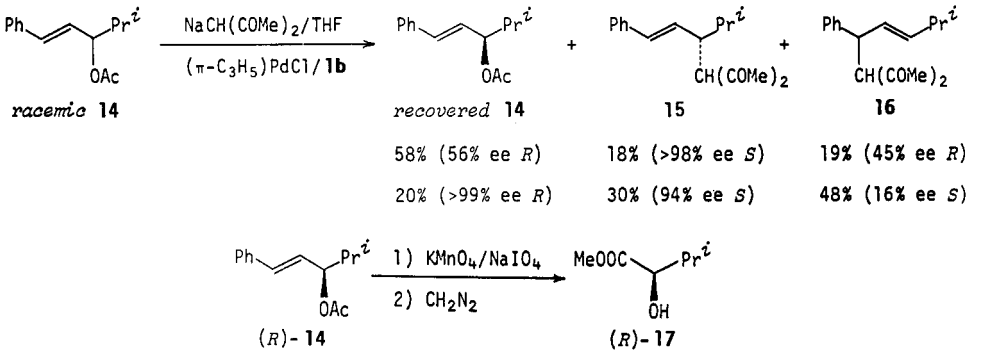
(S)-**11a**, respectively, and that on C-3 carbon of **12** and **13** will produce (S)-**10a** and (R)-**10a**, respectively, since the soft carbon nucleophiles including acetylacetonate anion have been demonstrated to attack the π-allyl carbon from the side opposite to palladium (ref. 13). The results obtained above that the reaction of racemic **9a** gave (S)-**10a** of 95% ee and (S)-**11a** of 80% ee in a ratio of 44/56 indicate that the products consist of (S)-10a (43%), (R)-10a (1%), (S)-**11a** (50%), and (R)-**11a** (6%). The ratios of the nucleophilic attack on the π-allyl carbons are calculated to be C-1/C-3 = 6/43 for **12** and 50/1 for **13**. The chiral ferrocenylphosphine **1b** is an effective ligand for the reaction of allyl acetates which proceeds via π-allylpalladium intermediate bearing meso π-allyl fragment (vide supra), and it has been observed that the ratios of the nucleophilic attack on the diastereotopic π-allyl carbons of palladium intermediates complexed with **1b** are 95/5 for 1,3-diphenyl-π-allyl and 93/7 for 1,3-di(3-methoxyphenyl)-π-allyl (see Table 1). The ratio of the nucleophilic attack is changed to 43/6 in **12** and 50/1 in **13** by steric factors of phenyl and 3-methoxyphenyl groups. The π-allyl carbon substituted with phenyl is more subject to the nucleophilic attack than that with 3-methoxyphenyl.

The enantiomeric purities of the alkylation products obtained in the reaction of allyl acetates substituted with phenyl and several other aryl groups, 1-naphthyl (**9b**), 4-chlorophenyl (**9c**), and 4-methylphenyl (**9d**) under the similar conditions are 94%, 75%, 87%, 70%, 86%, and 72% ee for **10b**, **11b**, **10c**, **11c**, **10d**, and **11d**, respectively. The ratio of the regioisomeric products **10**/**11** are between 46/54 and 45/55. It is noteworthy that the minor regioisomers **10** always had higher % ee values than the major ones as can be expected from the reaction mechanism, and that the regioselectivity of nucleophilic attack was not strongly dependent on the electronic nature of the aryl group. The regioselectivity seems to be controlled mainly by the steric bulkiness of the aryl substituents in all cases encountered.

A highly selective kinetic resolution of racemic allyl acetates was observed in the palladium-catalyzed asymmetric allylic alkylation (ref. 18). Racemic 1-[(E)-styryl]-2-methylpropyl acetate (**14**) was allowed to react with 0.5 equiv of sodium acetylacetonate in THF at 40 °C for 3 days in the presence of 1 mol% of the **1b**-palladium catalyst to give 58% of the recovered acetate **14** and 37% of allylic alkylation products consisting of 1-[(E)-styryl]-2-methylpropylacetylacetone (**15**) and its regioisomer **16** in a ratio of 48:52 (Scheme 7). The recovered acetate **14** was determined to be an (R) isomer of 56% ee by converting it into known (R)-(-)-methyl 2-hydroxy-3-methylbutanoate (**17**). The products **15** and **16** were found to be >98% ee and 45% ee, respectively, and their configurations were deduced to be (S) and (R), respectively, from the configuration of the consumed acetate, since the stereochemistry of the catalytic allylic alkylation has been established to be retention (ref. 19). The relative rate ratio of the enantiomer of the acetate **14** is calculated to be $k/k' = 14$ using the equation for the kinetic resolution (ref. 20), and it is expected that enantiomeric purity of the recovered substrate should exceed 99% at the conversion of 67%. Actually, the reaction carried to 80% conversion gave the acetate **14** of absolute optical purity (>99% ee), which was accompanied by the formation of 30% of (S)-**15** (94% ee) and 48% of (S)-**16** (16% ee). The high enantiomeric purity of one of the regioisomeric products regardless of the conversion can be also rationalized by the mechanism shown in the Scheme 6.

Use of sodium dimethyl malonate instead of acetylacetonate for the reaction of **14** resulted in a small decrease of the enantiomeric ratio ($k/k' = 6.6$). The ligand **1b** was also effective for the kinetic resolution of racemic [(E)-styryl]cyclohexylmethyl acetate ($k/k' = 7.0$) but was not effective for 1-[(E)-styryl]ethyl acetate ($k/k' = 1.2$).

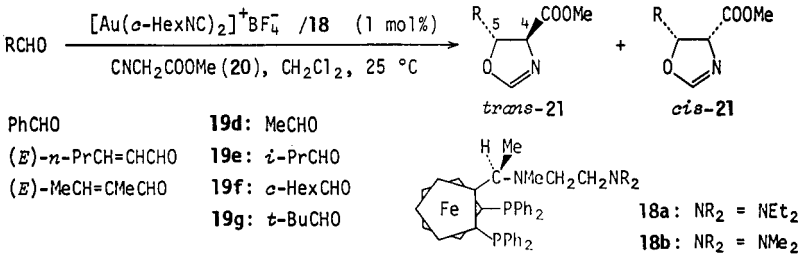
Scheme 7



ASYMMETRIC ALDOL REACTION OF ISOCYANOACETATE WITH ALDEHYDES

There has been great interest in the enantioselective aldol reactions of enolates with aldehydes to produce optically active β-hydroxycarbonyl compounds (ref. 21), but there have been few reports on the use of chiral catalysts for such reactions (ref. 22). Here we describe gold(I)-catalyzed asymmetric aldol reaction of an isocyanoacetate with aldehydes producing optically active 5-alkyl-2-oxazoline-4-carboxylates with high enantio- and diastereoselectivity (Scheme 8) which are useful synthetic intermediates to optically active β-hydroxyamino acids and their derivatives (ref. 23).

Scheme 8



We have found, in numerous studies, that the gold complex generated in situ by mixing bis-(cyclohexyl isocyanide)gold(I) tetrafluoroborate and (R)-N-methyl-N-[2-(dialkylamino)ethyl]-1-[(S)-1',2-bis(diphenylphosphino)ferrocenyl]ethylamine (18) (ref. 10) is an effective catalyst for the reaction of various types of aldehydes **19** with methyl isocyanoacetate (**20**). Reaction of benzaldehyde (**19a**) with **20** in the presence of 1 mol% of the cationic gold catalyst complexed with the ferrocenylphosphine **18a** in dry dichloromethane at 25 °C for 20 h gave 95% yield of 4-methoxycarbonyl-5-phenyl-2-oxazoline (**21a**) (trans/cis = 89/11). The enantiomeric purities of trans-**21a** and cis-**21a** were determined to be 96% ee and 49% ee, respectively, by ^{1}H NMR studies using a chiral europium shift reagent. The trans-**21a** was converted in high yields into known L-(-)-threo-β-phenylserine and (1R,2R)-(-)-1-phenyl-2-amino-1,3-propandiol via methyl phenylserinate. Therefore, (+)-trans-**21a** has the configuration of (4S,5R). Epimerization of (-)-cis-**21a** at C-4 with triethylamine in refluxing benzene gave (4S,5R)-trans-21a, indicating that the configuration of (-)-cis-21a is (4R,5R).

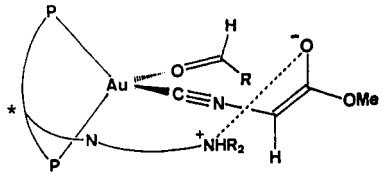
Representative results summarized in Table 2 were obtained under similar conditions. High enantioselectivity (>90%) and high trans selectivity (>97%) were observed in the reaction of secondary and tertiary alkyl aldehydes **19e**, **19f**, and **19g**. The gold catalyst was also effec-

Table 2. Reaction of Aldehydes **19** with Isocyanoacetate **20** Catalyzed by the Chiral Ferrocenylphosphine-Gold Complex.[a]

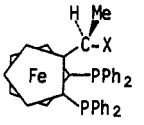
aldehyde **19**	ligand **18**	yield[b](%) of **21**	ratio of trans/cis	trans-**21** % ee	cis-**21** % ee
PhCHO (**19a**)	**18a**	98	89/11	96 (4S,5R)	49 (4R,5R)
	18b	91	90/10	94 (4S,5R)	4 (4S,5S)
(E)-n-PrCH=CHCHO (**19b**)	**18a**	83	81/19	84 (4S,5R)	52 (4R,5R)
	18b	97	80/20	87 (4S,5R)	0
(E)-MeCH=CMeCHO (**19c**)	**18b**	89	91/9	95 (4S,5R)	31 (4R,5R)
MeCHO (**19d**)	**18a**	100	84/16	72 (4S,5R)	44 (4R,5R)
i-PrCHO (**19e**)	**18a**	99	98/2	92 (4S,5R)	
c-HexCHO (**19f**)	**18a**	95	97/3	90 (4S,5R)	
	18b	96	98/2	81 (4S,5R)	
t-BuCHO (**19g**)	**18a**	100	100/0	97 (4S,5R)	

[a] The reaction was carried out in dichloromethane at 25 °C for 20-40 h. **19**/**20**/catalyst = 1.1/1.0/0.01. [b] Isolated yield by distillation based on **20**.

tive for the reaction of α,β-unsaturated aldehydes **19b** and **19c** to give the corresponding oxazolines of 87% ee and 95% ee, respectively. The high efficiency of the ferrocenylphosphine ligand **18** may be visualized by the transition state **A** where the dialkylamino group at the end of the side chain on **18** participates in the formation of enolate of isocyanoacetate coordinated with gold. It is probable that the participation may permit a favorable arrangement of the enolate and aldehyde on the gold(I) at the diastereomeric transition state to bring about high stereoselectivity. Use of the phosphine ligand **22** which is analogous to **18a** but with 3-(diethylamino)propyl side chain resulted in the formation of **21a** with 26% ee, indicating that the distance between the amino group and the ferrocene moiety is of crucial importance for the selectivity. The ferrocenylphosphine BPPFA (**2a**) which lacks the side chain, as well as chiraphos (ref. 24), DIOP (ref. 14), and p-TolBINAP (ref. 25), gave almost racemic oxazolines. It should be noted that the use of gold is essential for the high selectivity, silver or copper catalyst being much less selective. This may be ascribed to the stronger affinity of gold(I) to phosphorus atoms. The ligand **18** can coordinate to gold with two phosphorus atoms leaving two nitrogen atoms free while silver or copper forms undesirable species by coordination of **18** with nitrogen atom(s) instead of phosphorus.

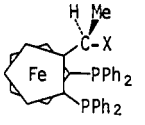


A



22: X = $NMe(CH_2)_3NEt_2$

2a: X = NMe_2 (BPPFA)



23: X = $NMeCH_2CH_2N$O

$NMeCH_2CH_2N$

Further modification of the ferrocenylphosphine ligands by introducing 2-morpholino or piperidino group at the terminal position of the ferrocene side chain improved both enantio- and diastereoselectivity. The ratios of trans-**21**/cis-**21** and enantiomeric purities of trans-**21** obtained in the reaction with gold-(R)-(S)-**23** catalyst are as follows: PhCHO; 95/5, 98% ee. Piperonal; 96/4, 98% ee. (E)-n-PrCH=CHCHO; 87/13, 95% ee. MeCHO; 93/7, 90% ee. i-PrCHO; >99/1, 96% ee.

REFERENCES

1. Reviews: H.B. Kagan and J.C. Fiaud, Top. Stereochem. 10, 175-285 (1978). B. Bosnich and M.D. Fryzuk, Top. Stereochem. 12, 119-154 (1981). T.Hayashi and M. Kumada, "Asymmetric Synthesis," ed by J.D. Morrison, Academic Press, Inc. New York (1985), Vol. 5, Chap. 5.
2. T. Hayashi and M. Kumada, Acc. Chem. Res. 15, 395-401 (1982).
3. T. Hayashi, T. Mise, S. Mitachi, K. Yamamoto and M. Kumada, Tetrahedron Lett. 1133-1134 (1976). T. Hayashi, K. Kanehira and M. Kumada, Tetrahedron Lett. 22, 4417-4420 (1981).
4. T. Hayashi, T. Mise and M. Kumada, Tetrahedron Lett. 4351-4354 (1976). T. Hayashi, A. Katsumura, M. Konishi and M. Kumada, Tetrahedron Lett. 425-428 (1979).
5. T. Hayashi, K. Kabeta, T. Yamamoto, K. Tamao and M. Kumada, Tetrahedron Lett. 24, 5661-5664 (1983). T. Hayashi and K. Kabeta, Tetrahedron Lett. 26, 3023-3026 (1985).
6. T. Hayashi, M. Tajika, K. Tamao and M. Kumada, J. Am. Chem. Soc. 98, 3718-3719 (1976). T. Hayashi, M. Konishi, M. Fukushima, T. Mise, M. Kagotani, M. Tajika and M. Kumada, J. Am. Chem. Soc. 104, 180-186 (1982). T. Hayashi, T. Hagihara, Y. Katsuro and M. Kumada, Bull. Chem. Soc. Jpn. 56, 363-364 (1983).
7. T. Hayashi, M. Konishi, H. Ito and M. Kumada, J. Am. Chem. Soc. 104, 4962-4963 (1982). T. Hayashi, M. Konishi, Y. Okamoto, K. Kabeta and M. Kumada, J. Org. Chem. 51, 3772-3781 (1986).
8. T. Hayashi, K. Kanehira, T. Hagihara and M. Kumada, submitted for publication.
9. D. Marquarding, H. Klusacek, G. Gokel, P. Hoffmann and I. Ugi, J. Am. Chem. Soc. 92, 5389-5393 (1970).
10. T. Hayashi, T. Mise, M. Fukushima, M. Kagotani, N. Nagashima, Y. Hamada, A. Matsumoto, S. Kawakami, M. Konishi, K. Yamamoto and M. Kumada, Bull. Chem. Soc. Jpn. 53, 1138-1151 (1980).
11. T. Hayashi, K. Kanehira, H. Tsuchiya and M. Kumada, J. Chem. Soc., Chem. Commun. 1162-1164 (1982).
12. T. Hayashi, A. Yamamoto, T. Hagihara and Y. Ito, Tetrahedron Lett. 27, 191-194 (1986).
13. T. Hayashi, M. Konishi and M. Kumada, J. Chem. Soc., Chem. Commun. 107-108 (1984), and references cited therein.
14. H.B. Kagan and T.P. Dang, J. Am. Chem. Soc. 94, 6429-6433 (1972).
15. K. Achiwa, J. Am. Chem. Soc. 98, 8265 (1976).
16. T. Hayashi, A. Yamamoto and Y. Ito, Chem. Lett. 177-180 (1987).
17. T. Hayashi, T. Hagihara, M. Konishi and M. Kumada, J. Am. Chem. Soc. 105, 7767-7768 (1983)
18. T. Hayashi, A. Yamamoto and Y. Ito, J. Chem. Soc., Chem. Commun. 1090-1092 (1986).
19. T. Hayashi, A. Yamamoto and T. Hagihara, J. Org. Chem. 51, 723-727 (1986).
20. C.S. Chen, Y. Fujimoto, G. Girdaukas and C.J. Sih, J. Am. Chem. Soc. 104, 7294 (1982), and references cited therein.
21. Reviews: C.H. Heathcock, "Asymmetric Synthesis," ed by J.D. Morrison, Academic Press, Inc. New York (1984), Vol. 3, Chap. 2. D.A. Evans, J.V. Nelson and T.R. Taber, Top. Stereochem. 13, 1 (1982).
22. M. Nakagawa, H. Nakao and K. Watanabe, Chem. Lett. 391-394 (1985).
23. Y. Ito, M. Sawamura and T. Hayashi, J. Am. Chem. Soc. 108, 6405-6406 (1986).
24. M.D. Fryzuk and B. Bosnich, J. Am. Chem. Soc. 99, 6262 (1977).
25. H. Takaya, K. Mashima, K. Koyano, M. Yagi, H. Kumobayashi, T. Taketomi, S. Akutagawa and R. Noyori, J. Org. Chem. 51, 629 (1986).