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ASYMMETRIC CATALYTIC HYDROSILYLATION OF KETONES
PREPARATION OF CHIRAL FERROCENYLPHOSPHINES AS CHIRAL LIGANDS

Tamio Hayashi, Keiji Yamamoto, and Makoto Kumada*
Department of Synthetic Chemistry, Kyoto University, Yoshida, Kyoto 606, Japan

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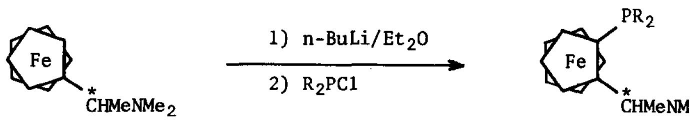
Asymmetric syntheses, especially hydrogenation, catalyzed by transition metal complexes with chiral ligands have recently attracted much interest. In most cases, phosphines having an asymmetric center at the phosphorus atom[1] or those derived from *L*-threitol[2] or *l*-menthol[3] have been successfully used as chiral ligands.

We wish to report the preparation of new phosphines with planar chirality which arises from introducing phosphino groups into α-dimethylaminoethylferrocene, and the use of these phosphines as chiral ligands in asymmetric catalytic hydrosilylation of ketones with which we have been primarily concerned.[4]

Chiral ferrocenylphosphines are readily prepared by way of stereoselective lithiation of (*S*)-α-ferrocenylethyldimethylamine(1).[5] Thus, 1 (14 mmoles) was metalated with n-butyllithium (17 mmoles) in ether at room temperature, and the mixture was then treated with chlorodiphenylphosphine (28 mmoles) to give (*S*)-α-[(*R*)-2-diphenylphosphinoferrocenyl]ethyldimethylamine(PPFA). The product was purified by alumina-column chromatography (eluent n-hexane/benzene, 3:1) and recrystallization from ethanol: yield 50%; mp 139°; $[\alpha]_D^{25}$ +361° (c 0.6, ethanol). In a similar manner, (*R*)-α-[(*S*)-2-dimethylphosphinoferrocenyl]ethyldimethylamine(MPFA) was obtained starting with (*R*)-1 (eq. 1).

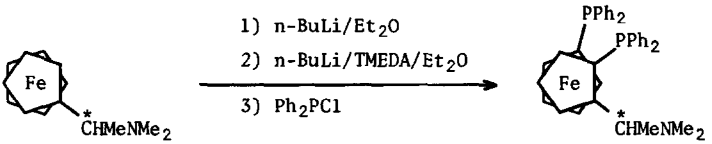


(1)

(*S*) or (*R*)-1

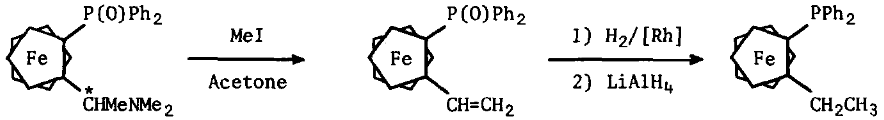
(*S*)-(*R*)-PPFA (R = Ph)
(*R*)-(*S*)-MPFA (R = Me)

Stepwise lithiation of (*S*)-**1** with n-BuLi in ether and with n-BuLi/TMEDA in ether led to the introduction of two diphenylphosphino groups into both the cyclopentadienyl rings to give (*S*)-α-[(*R*)-1',2-bis(diphenylphosphino)ferrocenyl]ethyldimethylamine(BPPFA) (eq. 2).



(*S*)-**1** (*S*)-(*R*)-BPPFA (2)

Finally, (*R*)-1-ethyl-2-diphenylphosphinoferrocene(EPPF) having only a planar element of chirality was prepared as shown in eq. 3.



(*R*)-EPPF (3)

All new compounds gave satisfactory elemental analyses and nmr spectra. Melting points and specific rotations of these chiral ferrocenylphosphines are summarized in Table 1. The absorption and circular dichroism (CD) spectra are shown in Figs. 1 and 2.

Table 1. Physical constants of chiral ferrocenylphosphines.

Abbr.	Mp (°C)	$[\alpha]_D^{25}$
(*S*)-(*R*)-PPFA	139	+361° (c 0.6, EtOH)
(*R*)-(*S*)-MPFA	oil	-134° (c 0.3, $CHCl_3$)
(*S*)-(*R*)-BPPFA	117.5	+345° (c 0.5, $CHCl_3$)
(*R*)-EPPF	94.5	+273° (c 0.3, $CHCl_3$)

The absorption spectrum of ferrocene has two long wavelength bands at 440 and 325 nm assignable to d-d type transition.[6] The CD spectra of chiral ferrocenylphosphines reveal optical activity arising from the planar chirality around these two absoption bands, that is, (*S*)-(*R*)-PPFA, (*S*)-(*R*)-BPPFA, and (*R*)-EPPF all have positive and negative Cotton effects around 450 ~ 470 and 340 ~ 350 nm respectively, whereas opposite Cotton effects are observed in the case of (*R*)-(*S*)-MPFA.

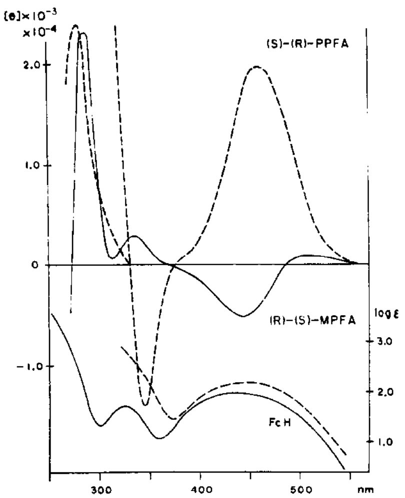


Fig. 1. CD and UV spectra of (*S*)-(*R*)-PPFA and (*R*)-(*S*)-MPFA in chloroform.

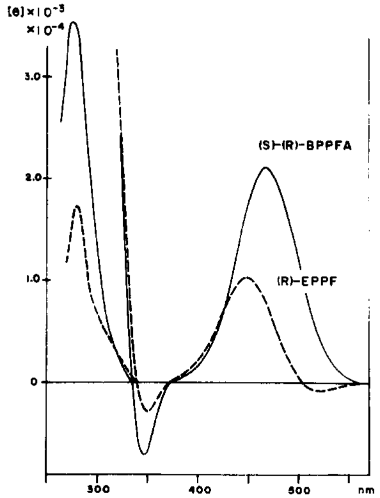


Fig. 2. CD spectra of (*S*)-(*R*)-BPPFA and (*R*)-EPPF in chloroform.

The asymmetric catalytic hydrosilylation of ketones[4] was carried out in the presence of rhodium complexes containing these chiral ferrocenylphosphines as ligands. The asymmetric

Table 2. Asymmetric Hydrosilylation of Ketones Catalyzed by Chiral Ferrocenylphosphine-Rhodium Complexes[a] at 20°.

Ketone	Silane	Ligand	Yield[b] (%)	Configuration	Optical Purity (%)
EtCOPh	$PhMe_2SiH$[c]	(*S*)-(*R*)-PPFA	61	*R*	10.5
EtCOPh	$PhMe_2SiH$[c]	(*S*)-(*R*)-PPFA[d]	40	*R*	9.0
t-BuCOMe	$PhMe_2SiH$[c]	(*S*)-(*R*)-PPFA	71	*R*	19.6
MeCOPh	Ph_2SiH_2	(*R*)-(*S*)-MPFA	89	*R*	49.2
EtCOPh	Ph_2SiH_2	(*R*)-(*S*)-MPFA	83	*R*	38.3
t-BuCOMe	Ph_2SiH_2	(*R*)-(*S*)-MPFA	74	*R*	41.1
t-BuCOMe	$PhMe_2SiH$[c]	(*R*)-(*S*)-MPFA	29	*S*	23.5
MeCOPh	Ph_2SiH_2	(*S*)-(*R*)-BPPFA	72	*R*	28.6
EtCOPh	Ph_2SiH_2	(*S*)-(*R*)-BPPFA	73	*R*	24.5
EtCOPh	Et_2SiH_2	(*S*)-(*R*)-BPPFA	84	*R*	25.3
EtCOPh	Me_3SiH[c]	(*R*)-EPPF	88	*R*	5.2

[a] [Rh]* = 0.05 mol%. [b] Isolated yield. [c] At 50°. [d] PPFA/Rh = 1.

additions of trialkylsilanes and dialkylsilanes readily took place at 50° and 20°, respectively (eq. 4). The results obtained are summarized in Table 2.

$$R^1COR^2 \quad + \quad R_3SiH \xrightarrow{[Rh]^*} R^1R^2\overset{*}{C}HOSiR_3 \qquad (4)$$

$$[Rh]^* : \frac{1}{2}[(C_6H_{10})RhCl]_2 \quad + \quad 2P^*$$

As is seen from Table 2, fairly good optical yields were attained when MPFA or BPPFA was used. For example, the reaction of acetophenone with diphenylsilane catalyzed by (*R*)-(*S*)-MPFA-Rh complex resulted in higher optical yield than the cases in which (*R*)-benzylmethylphenylphosphine or (-)-diop-Rh complex was used. The high ability of (*R*)-(*S*)-MPFA as an asymmetry inducing ligand was also found in the reaction of pinacolone.

In addition to the expected steric effects, attractive interactions between the amino group of the ligand and an appropriate prochiral substrate might contribute to the asymmetric potential of the reaction. Efforts toward this end as well as toward the asymmetric hydrogenation using these catalyst systems are under way.

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