

C₂-대칭성 키랄 Bis(imino)pyridine 리간드의 합성

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Synthesis of C₂-Symmetrical Chiral Bis(imino)pyridine Ligand

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During the past two decades, there has been considerable interest in catalytic asymmetric synthesis using a chiral ligand-transition metal complex catalyst¹. It is one of the most promising methods for synthesis of optically active compounds, since a large amount of optically active products are formed from a small amount of chiral materials. Common chiral ligands have been phosphines and extensively studied in a variety of catalytic application². Recent research of asymmetric hydrosilylation (Scheme 1) focuses on the use of nitrogen based ligands³⁻⁵.

Optically active Schiff base 1 has been used as a bidentate chiral ligand in the asymmetric hydrosilylation of prochiral ketones⁴. The very recent work of Nishiyama *et al.* has showed tridentate ligand bis(oxazolanyl)pyridine to be better than bidentate ligand in the reaction⁵. We have given

much attention to the synthesis of such chiral tridentate ligand like 4.

Here we report the synthesis of C₂-symmetrical and tridentate chiral Schiff base from 2,6-pyridinedicarboxaldehyde (Scheme 2).

Several methods are available for the oxidation of 2,6-pyridinedimethanol 2 to 2,6-pyridinedicarboxaldehyde 3⁶. Selenium dioxide was the best oxidizing agent. Treatment of 2 with 2.1 equiv. of SeO₂ in dioxane at 80°C for 4 h afforded 3 in 84% yield after recrystallization (hexane/chloroform=3/1). Optically active tridentate 2,6-bis(1-phenylethylimino)pyridines 4 having two imine skeleton would be easily synthesized through direct Schiff base condensation. Treatment of pyridinedicarboxaldehyde 3 with 2 equiv. of optically active (*R*)-1-phenylethylamine in refluxing benzene gave, after flash chromatography of the crude

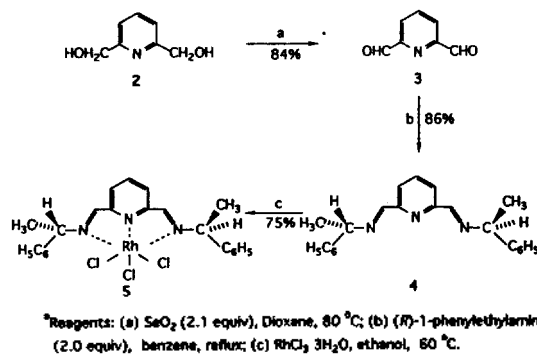
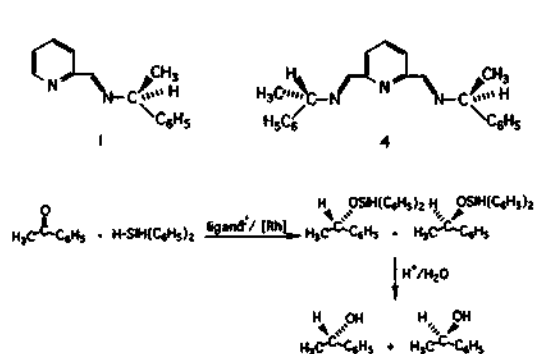


Table 1. Physical properties of compounds 4 and 5

Compd	mp.	$[\alpha]_D^{25}$ ($c=0.8$, CHCl ₃)	NMR (CDCl ₃), δ
4	oil	-1.2°	¹ H-NMR 1.62(d, $J=6.9$ Hz, 6H), 4.65(q, $J=6.5$ Hz, 2H), 7.24~7.46(m, 10H), 7.78(t, $J=8.3$ Hz, 1H), 8.13(d, $J=7.8$ Hz, 2H), 8.49(s, 2H)
5	182°C dec	-2.9°	¹ H 2.07(d, $J=6.9$ Hz, 6H), 6.12(q, $J=6.5$ Hz, 2H), 7.38~7.60(m, 10H), 7.64(s, 2H), 7.69(d, $J=7.9$ Hz, 2H), 8.03(t, $J=8.3$ Hz, 1H)

product, 4 as a colorless oil in ca. 86% yield. The tridentate chiral ligand 4 reacted with RhCl₃·3H₂O in ethanol at 60°C for 3 hr to afford Rh complex 5, which was purified by flash chromatography (ethyl acetate/methanol=7/1) to give stable orange solids in 75% yield.

The structural assignment for 4 and 5 are based upon ¹H-NMR spectral data. The spectral data are collected in Table 1. In particular, the protons of the CH=N groups exhibit characteristic low chemical shifts (4: $\delta=7.64$, 5: $\delta=8.49$)⁴.

Now we are examining the potential of this new ligand and the corresponding Rh complex in asy-

mmetric hydrosilylation of prochiral ketone.

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