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OPTICALLY ACTIVE 2,2'-BIS(DIPHENYLPHOSPHINOMETHYL)-1,1'-BINAPHTHYL: A NEW CHIRAL BIDENTATE PHOSPHINE LIGAND FOR TRANSITION-METAL COMPLEX CATALYZED ASYMMETRIC REACTIONS

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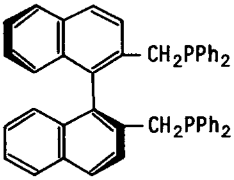
In recent years, transition-metal complex catalyzed asymmetric reactions have received much attention to obtain chiral molecules efficiently and considerable efforts have been devoted to developing new chiral phosphine ligands.[1] Two types of optically active phosphine ligands have so far been used for the catalytic asymmetric reactions. One contains a chiral center at the phosphorus atom, as in benzylmethylphenylphosphine (BMPP),[2] *o*-anisylcyclohexylmethylphosphine (ACMP),[3] and 1,2-di(*o*-anisylphenylphosphino)ethane,[4] and the other carries chiral carbon moieties; of the latter, 2,3-*O*-(isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP),[5] neomenthyldiphenylphosphine (NMDPP)[6] and (2*S*,4*S*)-*N*-butoxycarbonyl-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine (BPPM)[7] contain a central element of chirality at carbon, while ferrocenylphosphines such as α-[1',2-bis(diphenylphosphino)ferrocenyl]ethyldimethylamine (BPPFA)[8] possess a planar element of chirality as well. We have now prepared a new optically active bidentate phosphine ligand, 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthyl [hereafter abbreviated to NAPHOS(1,1)], which is the first member of a third class of chiral phosphines which carry an axial element of chirality only.

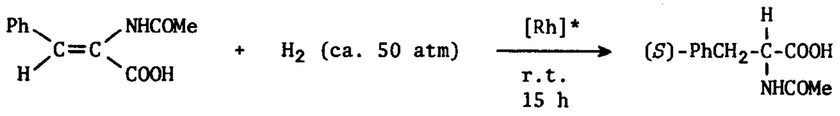


(*S*)-(-)-NAPHOS(1,1)

Racemic (±)-NAPHOS(1,1) has been obtained via the trichlorosilane-triethylamine reduction[2] of the corresponding NAPHOS(1,1) dioxide,[9] prepared by the Arbuzov reaction between 2,2'-bis-(bromomethyl)-1,1'-binaphthyl[10] and methyl diphenylphosphinite, as white needles, m.p. 160-161.5°C (in air) [*m/e* 650 (M^+, 14), 573 ($M-C_6H_5$, 8), 465 ($M-PPh_2$, 100)]. The crystals are almost air-stable, but solutions extremely air-sensitive. The ^1H NMR spectrum (100 MHz, $CDCl_3$) exhibits a methylene proton resonance at δ 3.21 as an unresolved broad signal, possibly indicative of an ABX pattern with small coupling constants.

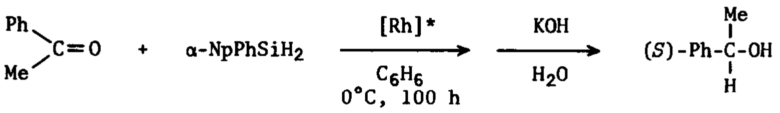
An optically active (*S*)-(-)-NAPHOS(1,1) dioxide, prepared from (*S*)-(-)-2,2'-bis(bromomethyl)-1,1'-binaphthyl, $[\alpha]_D^{23}$ -158.7°, $[\alpha]_{577}^{23}$ -164.9° (c 0.4, benzene) (97% optically pure),[10] showed $[\alpha]_D^{23}$ -152.1° (c 0.4, benzene), m.p. 235-238°C.[9] Similar reduction of the dioxide gave the optically active (*S*)-(-)-NAPHOS(1,1),[11] $[\alpha]_D^{25}$ -69.6° (c 0.5, benzene) as a glassy material.

Using this new chiral phosphine as a ligand, catalytic asymmetric hydrogenation,[12] hydrosilylation,[13] and Grignard cross-coupling[14,15] have been examined. The results are as follows.



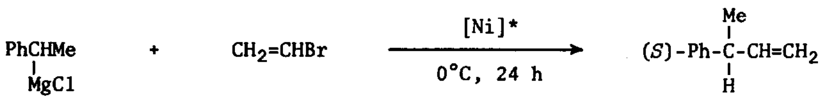
$$\mathrm{PhCH{=}C(NHCOMe)COOH} + H_2\ (\text{ca. 50 atm}) \xrightarrow[\text{r.t. 15 h}]{[Rh]^*} (S)\text{-}\mathrm{PhCH_2\text{-}CH(NHCOMe)\text{-}COOH}$$

$[\alpha]_D^{26}$ +24.9° (0.5, EtOH) 54% ee



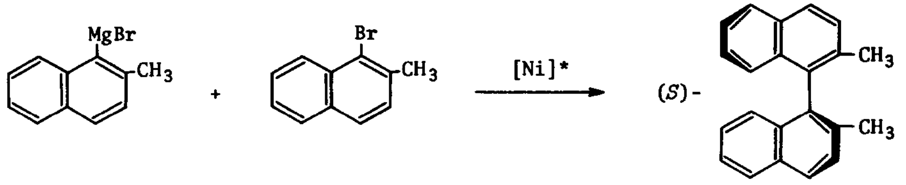
$$\mathrm{PhC(Me){=}O} + \alpha\text{-}\mathrm{NpPhSiH_2} \xrightarrow[C_6H_6,\ 0°C,\ 100\ h]{[Rh]^*} \xrightarrow[H_2O]{KOH} (S)\text{-}\mathrm{Ph\text{-}CH(Me)\text{-}OH}$$

$[\alpha]_D^{20}$ +7.68° (neat) 18% ee



$$\mathrm{PhCH(Me)MgCl} + \mathrm{CH_2{=}CHBr} \xrightarrow[0°C,\ 24\ h]{[Ni]^*} (S)\text{-}\mathrm{Ph\text{-}CH(Me)\text{-}CH{=}CH_2}$$

$[\alpha]_D^{22}$ -0.73° (neat) 11% ee



$[\alpha]_D^{22.5}$ +2.62° (c 1.5, MeOH)

12.5% ee

$[Rh]^*$ = $[(1,5\text{-hexadiene})RhCl]_2/2$(*S*)-(-)-NAPHOS(1,1)

$[Ni]^*$ = $NiCl_2/$(*S*)-(-)-NAPHOS(1,1)

While NAPHOS(1,1) did not bring about satisfactorily high stereoselectivity in the first three reactions, for the last reaction it afforded the highest optical yield ever reported.[15] These results reveal the usefulness of this new class of chiral phosphine ligands. Our efforts are being devoted to the further development of new related axially chiral biaryl phosphines by making appropriate structural modifications.

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