Chiral Diene Ligands for Asymmetric Catalysis

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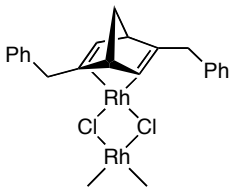
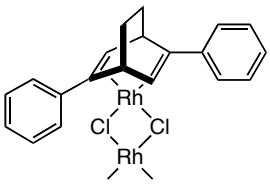
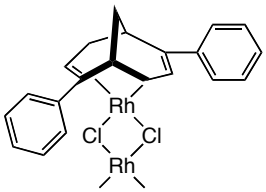
As conceptually new chiral ligands, we have been developing enantiomerically pure C_2-symmetric chiral dienes, whose basic diene skeleton is bicyclo[2.2.1]hepta-2,5-diene (nbd*), bicyclo[2.2.2]octa-2,5-diene (bod*), or bicyclo[3.3.1]nona-2,6-diene (bnd*). They have two alkyl or aryl substituents on the double bonds, one on each of the two double bonds. The chiral diene ligands were found to be better than the conventional chiral ligands represented by chiral bisphosphines in terms of both catalytic activity and enantioselectivity in some of the catalytic asymmetric reactions. Their high performance was observed in rhodium-catalyzed asymmetric addition of organoboron reagents to α,β-unsaturated ketones, *N*-sulfonylimines, and so on.[1]



(*R*,*R*)-Bn-nbd*

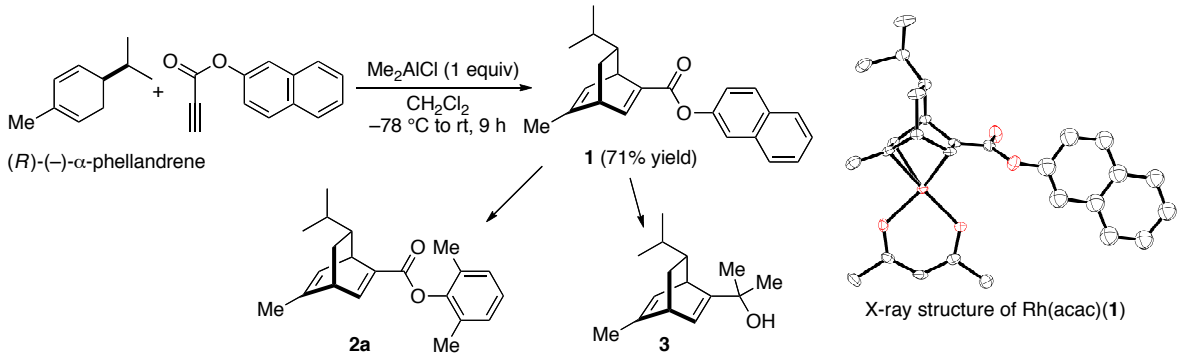


(*R*,*R*)-Ph-bod*



(*R*,*R*)-Ph-bnd*

Recently, we have developed a simple one-step synthesis of chiral dienes through the [4+2] cycloaddition of (*R*)-α-phellandrene with 2-naphthyl acetylenecarboxylate. The cycloaddition product **1** can be used as a chiral ligand as it is, and if it is required the 2-naphthyl ester moiety is readily converted, for example, into other esters **2** by ester exchange reactions. They were found to be excellent chiral ligands for the rhodium-catalyzed asymmetric addition reactions[2] including the conjugate addition to β,β-disubstituted α,β-unsaturated ketones and esters.



(*R*)-(–)-α-phellandrene

1 (71% yield)

2a

3

X-ray structure of Rh(acac)(**1**)

References

1. For a review: R. Shintani, T. Hayashi, *Aldrichimica Acta* **2009**, *42*, 31.
2. (a) R. Shintani, Y. Tsutsumi, M. Nagaosa, T. Nishimura, T. Hayashi, *J. Am. Chem. Soc*. **2009**, *131*, 13588. (b) R. Shintani, M. Takeda, T. Tsuji, T. Hayashi, *J. Am. Chem. Soc.* **2010**, *132*, 13168. (c) T. Nishimura, A. Noishiki, G. C. Tsui, T. Hayashi, *J. Am. Chem. Soc.* **2012**, *134*, 5056. (d) T. Nishimura, Y. Takiguchi, T. Hayashi, *J. Am. Chem. Soc*. **2012**, *134*, 9086. (e) T. Nishimura, A. Noishiki, T. Hayashi, *Angew. Chem. Int. Ed.* **2013**, *52*, 1777.