SYNLETT Spotlight 43

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

1,2-Bis-*N*-[2'-(diphenylphosphino)-benzo/naphtho]-1,2-diamino-cyclohexane – Trost Modular Ligands

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Introduction

Over the past ten years Trost et al. have developed a modular approach to ligand design for the Pd-catalysed asymmetric allylic alkylation (AAA) reaction. Much attention has focused on ligands such as **1a** and its variant **1b** which, under appropriate conditions, provide outstanding selectivity in a broad range of Pd-catalysed reactions.^{1,2} It should be noted that the mode of ligand bonding is not exclusively P,P-chelating, as in complexes **2a** and **2b**, and that ligand coordination is non-C₂-symmetric.³ Applications and uses of **1a** and **1b** are described.

Figure

Abstracts

The regioselective 1:1 hydroamination of dienes affords allylic amines in excellent yields. The reaction is broad for a wide range of anilines and proceeds with high enantioselectivity when the naphtho modular ligand **1b** is employed.⁴

a. [Pd(π -allyl)Cl]₂ (5 mol%),
Ligand **1a** or **1b** (11 mol%), THF, rt

Lig.	R	Yield	ee
1a	Ph	65	11
1b	Ph	87	89
1b	<i>p</i> -MeC ₆ H ₄	78	86
1b	<i>p</i> -EtO ₂ CC ₆ H ₄	83	95
1b	<i>p</i> -F ₃ CC ₆ H ₄	73	95

The Pd-catalysed AAA reaction of a range of nitroalkanes with acyclic and cyclic allyl esters, employing ligand **1a**, proceeds in high yields and enantioselectivities providing that catalyst loadings are low.^{3,5}

a. Pd₂dba₃·CHCl₃, **1a**, (C₄H₉)₄NCl, BSA,
RNO₂ (R = Me, Et), CH₂Cl₂, rt

The Pd-catalysed desymmetrisation of meso diesters is a proven and highly versatile method for providing monosubstituted products of high ee.^{2,6}

References

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