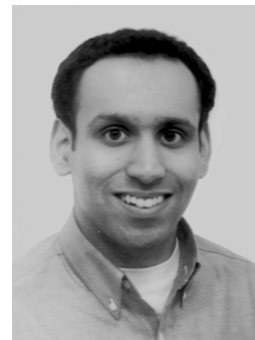


SYNLETT Spotlight 18

Asymmetric Catalysts Containing Phosphinoxazoline Ligands

Compiled by Neel K. Anand



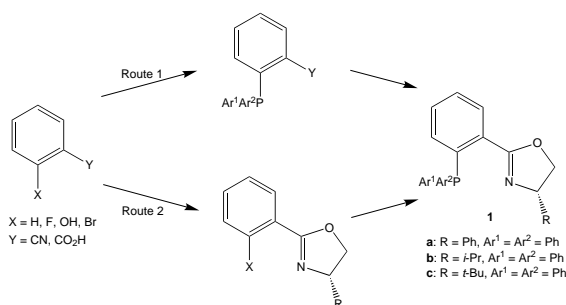
This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Laboratorium für Organische Chemie, ETH-Zürich, Universitätsstrasse 16, CH-8092 Zürich, Switzerland

Neel K. Anand was born in Derby, UK in 1974. He obtained a D.Phil. degree in 1999 from the University of Oxford for research involving biomimetic total synthesis, under the supervision of Professor Sir Jack Baldwin, FRS. He is currently engaged in post-doctoral work involving synthetic methodology with Professor Erick M. Carreira at the ETH-Zürich.

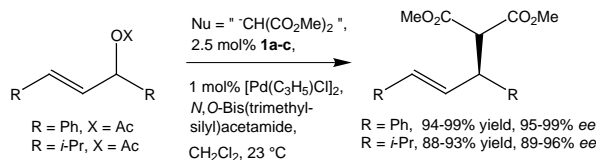
The unsymmetrical phosphinoxazolines **1** constitute one family of the newest generation of chiral bidentate ligands.¹ These ligands possess a chiral centre on the oxazoline portion and have the opportunity to incorporate a chiral *P*-centre. As part of a metal complex, the soft donor *P*-atom is a π -electron acceptor, unlike the hard donor *N*-atom. Stereoelectronic 'trans-influence' dictates that the atom complexed to the metal centre *trans* to the *P*-atom is significantly more electrophilic than the one located *trans* to the *N*-atom; thus regioselectivity of reactions is inherently increased by the electronic properties of the ligand. To date, the most promising complexes that contain these ligands contain a Cu, W, Pd, Pt, Ru or Ir centre and have been shown to catalyse a variety of reactions (including hydrogenation of ketones, olefins and imines;²⁻⁴ Diels-Alder reaction⁵) in high yield and enantiomeric excess.

Preparation: Either of two modular routes provide the opportunity to efficiently synthesise extensively varied phosphinoxazoline ligands **1** in no more than three steps from commercially available material.⁶ The asymmetric metal complex catalysts are generated in situ in the relevant reaction.

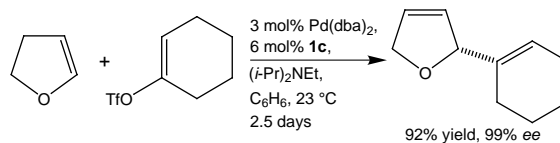


Abstracts

(a) Good enantioselectivity has been achieved when using **1** complexed to Pd,^{7,8} W,⁹ Ir¹⁰ or Pt¹¹ to catalyse allylic substitution reactions using a variety of nucleophiles (Nu) and allylic substrates (including examples containing non-identical R groups).



(b) **1c** has proved to be an efficient ligand for the enantioselective Heck reaction. Examples of carbocycles and *O*- and *N*-heterocycles reacting with aryl and cycloalkenyl triflates have been reported. High selectivity due to the low extent of C-C double bond migration in the heterocyclic ring of the product is notable.¹²



References and Notes

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