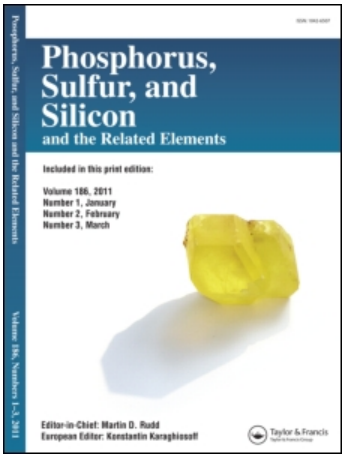

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

1-Phosphanorbornadienes in Enantioselective Catalysis

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Online publication date: 27 October 2010

To cite this Article Robin, Frederic , Lelièvre, Stephane , Mercier, Franc¸ois , Ricard, Louis and Mathey, Franc¸ois(2002) '1-Phosphanorbornadienes in Enantioselective Catalysis', Phosphorus, Sulfur, and Silicon and the Related Elements, 177: 6, 1371 — 1374
To link to this Article: DOI: 10.1080/10426500212222
URL: http://dx.doi.org/10.1080/10426500212222

Phosphorus, Sulfur and Silicon, 2002, Vol. 177:1371–1374

1042-6507/02 $12.00 + .00
DOI: 10.1080/10426500290093685

1-PHOSPHANORBORNADIENES IN ENANTIOSELECTIVE CATALYSIS

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(Received July 29, 2001; accepted December 25, 2001)

*Recent developments in the chemisty of 1-phosphanorbornadienes are reviewed. Due to their bicyclic structure with a non-racemisable phosphorus atom at the bridgehead, they are ideally suited to enantioselective catalysis as transition metal complexes. Amongst this family, two enantiopure species play a special role, i.e., the so-called BIPNOR, a 2,2′-bis-1,1′-phosphanorbornadienyl (**1**), and a 2-formyl-1-phosphanorbornadiene (**2**). BIPNOR displays high enantioselectivities for a range of rhodium-catalyzed reactions. The carboxyaldehyde (**2**) is an ideal starting point for the synthesis of a series of enantiopure chelating 1-phosphanorbornadienes whose structures can be optimized for various catalytic enantioselective reactions. Examples of both approaches are given.*

Keywords: Enantioselective catalysis; phosphanorbornadienes; phospholes

RESULTS AND DISCUSSION

Enantiopure phosphines whose chiral information is located at phosphorus play an increasingly important role in transition metal-mediated enantioselective catalysis.[1] This chiral information is relatively stable under ordinary "academic" conditions, but several mechanisms, i.e., pyramidal inversion, Berry pseudorotation, or edge inversion, can cause racemisation under the more stringent conditions used in industry (e.g., high TON, high rates requiring some heating, recycling of the catalysts). In such a context, there is a real need to

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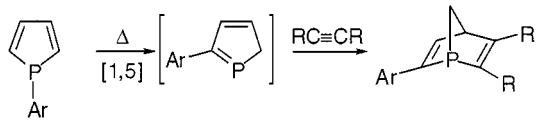
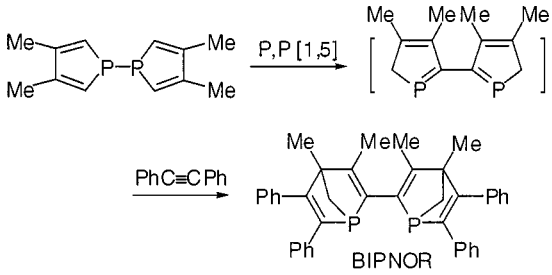
synthesize non-racemisable chiral phosphines. Bicyclic structures with phosphorus at the bridgehead represent a possible solution. In this category, 1-phosphanorbornadienes deserve special attention since they are easily accessible from phospholes and can be obtained with a large variety of substitution patterns (Scheme 1).[2]



SCHEME 1

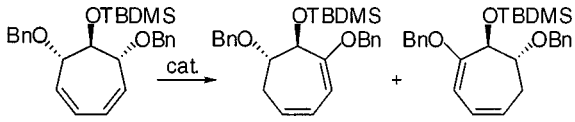
An early attempt with an enantiopure monodentate 1-phosphanorbornadiene proved to be disappointing with a maximum e.e. of 50% in the asymmetric hydrogenation of dehydroaminoacids.[3] The problem was thus to find a realistic access to a chelating 2,2′-bis-(phosphanorbornadienyl) structure. The solution, as depicted in Scheme 2, was found some time later.[4]



SCHEME 2

The resolution was initially carried out with enantiopure cyclopalladated complexes according to the technique of Wild.[5] It is currently performed on the P,P-dioxide using a chiral stationary phase. A series of preliminary asymmetric hydrogenation experiments of functional C=C and C=O double bonds proved that BIPNOR is very efficient in rhodium-catalysed processes but performs less satisfactorily with ruthenium (II). We investigated in some depth the case of a rhodium-catalyzed isomerisation of a cyclic diene in conjunction with the synthesis of calystegines[6] (Scheme 3).

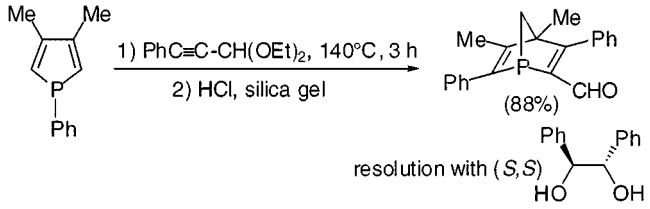
An e.e. as high as 92% was obtained with [Rh(BIPNOR)(cod)]PF_6 in toluene: DME. E.e. increases with temperature, as has been already found for entropy-controlled reactions.[7] In that precise case, BIPNOR



SCHEME 3

was found to be systematically superior to BINAP in terms of e.e.'s. The mechanism is thought to involve a η^5-pentadienylrhodium hydride.

In parallel, we devised an easy access to enantiopure phosphanorbornadiene-2-carboxaldehydes[8] (Scheme 4).



SCHEME 4

From these aldehydes, a whole range of functional chelating ligands are currently being built. At this point, the work of Gilbertson on phosphanorbornadieneoxazolines for use in a palladium-catalyzed allylic coupling or Heck reaction must be mentioned.[9] Our objective is now to synthesize a whole library of enantiopure phosphanorbornadiene ligands whose structures will be optimized according to the nature of the enantioselective catalytic reactions.

ACKNOWLEDGMENTS

This work has been continuously funded by Rhodia S. A. for several years.

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