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Journal of Organometallic Chemistry 577 (1998) 117–120

Journal of Organometallic Chemistry

From 2*H*-phospholes to BIPNOR, a new efficient biphosphine for asymmetric catalysis

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Received 19 May 1997

Abstract

For many years now, we have studied the 1*H*-/2*H*-phosphole equilibrium and its synthetic applications. On reaction with alkynes, 2*H*-phospholes yield the corresponding 1-phosphanorbornadienes. As ligands of rhodium(I), these phosphines show some potential in catalytic hydrogenation and hydroformylation of alkenes. Starting from 3,3′,4,4′-tetramethyl-1,1′-biphospholyl and tolan, we have similarly obtained the corresponding 2,2′-bis-(1-phosphanorbornadienyl) (BIPNOR) with two chiral, non-racemisable, phosphorus atoms at the bridgeheads. The pure enantiomers of BIPNOR appear to be efficient ligands in asymmetric hydrogenation of C=C and C=O double bonds.

Keywords: [1,5] sigmatropic shifts; [4 + 2] cycloadditions; enantioselective catalysis

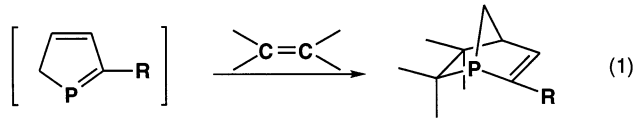
1. Introduction

While studying systematically the Diels–Alder reactivity of phospholes, we discovered in 1981 the equilibrium between 1*H*- and 2*H*-phospholes [1] (Scheme 1).

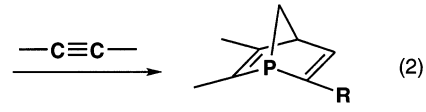
The origin of this equilibrium lies in the σ,π overlap between the P–R exocyclic bond and the dienic system. The migration of R depends heavily on the nature of R. Hydrogen migrates below 0°C [2] whereas sp-carbon substituents migrate around 100°C and sp^2-carbon substituents around 140°C [3]. Silicon, phosphorus and sulphur substituents also migrate. Oxygen does not result from the high strength of the P–O bond. Bachrach has shown that 1*H*-, 2*H*- and 3*H*-phospholes are close in energy but the activation barrier between 1*H* and 2*H* is low (*DH* 16 kcal mol^{-1}) whereas it is high between 2*H* and 3*H* (*DH* 27 kcal mol^{-1}) [4]. These data explain why 3*H*-phospholes do not contribute to the reactivity of phospholes under normal circumstances.

2. Reactivity of 2*H*-phospholes: a brief overview

From a practical standpoint, the most interesting reactions of these unstable 2*H*-phospholes are those where they act as very reactive 1-phosphadienes giving [4 + 2] cycloadducts with alkenes and alkynes [1,5] (Eqs. (1) and (2))



(1)



(2)

and those where they act as sources of aromatic phospholide ions and η^5-phospholyl complexes. In the latter case, the most recent applications concern the first practical synthesis of α-functional phospholide ions [6]

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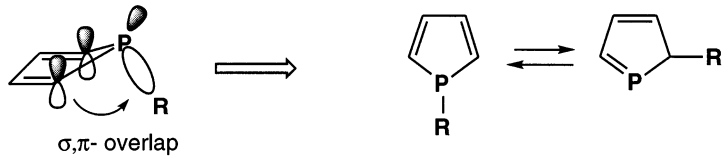
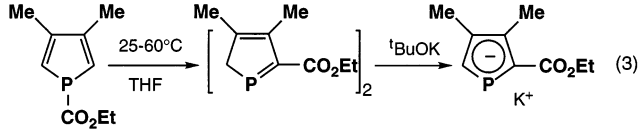
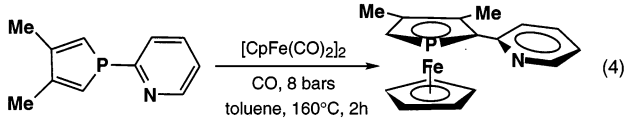


Scheme 1. The 1*H*-↔2*H*-phosphole equilibrium.

(Eq. 3) and the straightforward preparation of a chelating 2-(2′-pyridyl)phosphaferrocene [7] (Eq. 4).

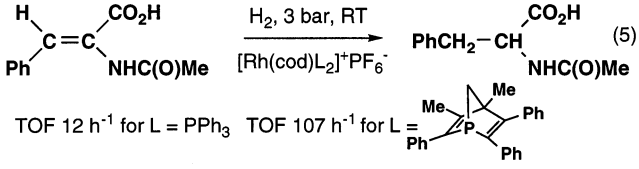




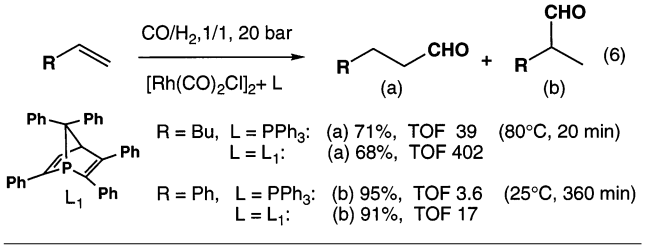
However, the outcome of this chemistry in homogeneous catalysis is exclusively centered around the robust and easily accessible 1-phosphanorbornadienes (Eq. 2).

3. From 1-phosphanorbornadienes to BIPNOR

These new 1-phosphanorbornadienes rapidly proved to be excellent ligands of rhodium for the catalytic hydrogenation of functional alkenes [8] (Eq. 5),

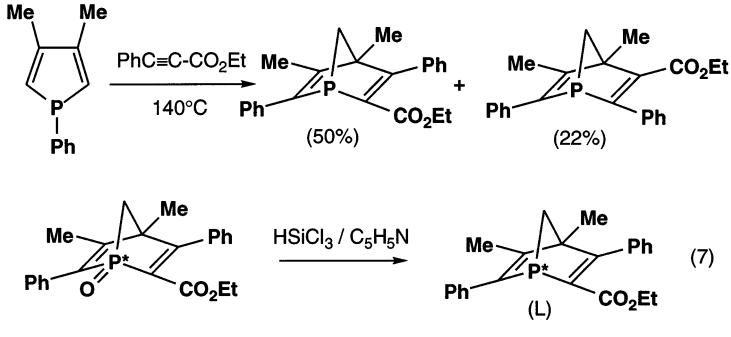


and the catalytic hydroformylation of terminal alkenes [9] (Eq. 6).

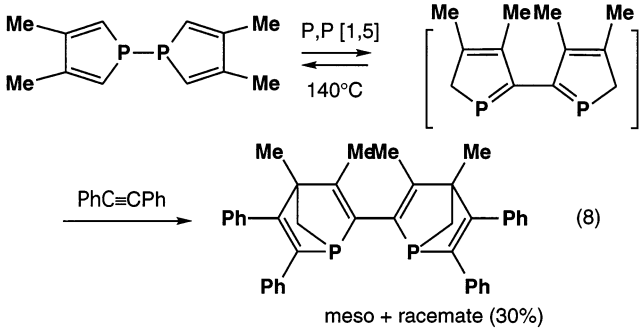


More recently, Herrmann et al. [10] prepared a sulphonated version of the phosphanorbornadiene of Eq. 5. This water-soluble species shows exceptional quality in the biphasic hydroformylation of propene. In such a context, looking for possible applications of homochiral 1-phosphanorbornadienes in asymmetric catalysis was an obvious choice.

Most of the homochiral bisphosphines currently in use in enantioselective catalysis carry the chiral information on their carbon backbone (BINAP [11], DuPHOS [12]...). With the only notable exception of DIPAMP [13], the chiral information is seldom carried by the phosphorus centre. Such a situation is nevertheless intuitively attractive since in that case, the transfer of chirality from the inductor to the product is favoured by their close proximity within the coordination sphere of the transition metal. The main drawback is that P-homochiral phosphines tend to racemise by a variety of routes including the pyramidal inversion, the Berry pseudorotation and the edge inversion [14]. Berry pseudorotation can easily occur in protic media whereas edge inversion does not necessitate the decoordination of phosphorus from the transition metal. In 1-phosphanorbornadienes, the phosphorus atom is located at the bridgehead position of a bicyclic system and none of the racemisation pathways can operate. From that standpoint, 1-phosphanorbornadienes are definitively superior to any other classical phosphines. We first investigated the synthesis of a monodentate homochiral species. The reaction of ethyl phenylpropiolate with a 2*H*-phosphole afforded the corresponding α- and β-functional phosphanorbornadienes whose separation was performed on silica gel. The two α-enantiomers were separated on a chiral phase as their P-oxides [15] (Eq. 7).

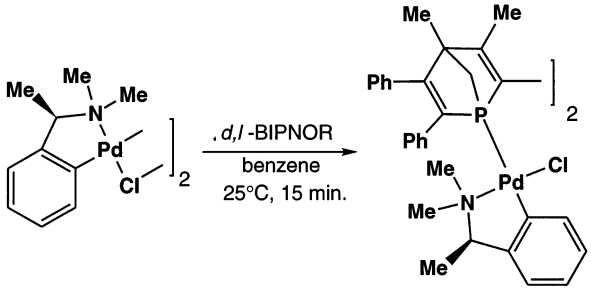


A 50% ee was observed in the rhodium-catalyzed asymmetric hydrogenation of a typical dehydroaminoacid. The next step was the discovery of a simple access to a 2,2′-*bis*-(1-*p*hospha*nor*bornadienyl) (BIPNOR)[16] (Eq. 8).



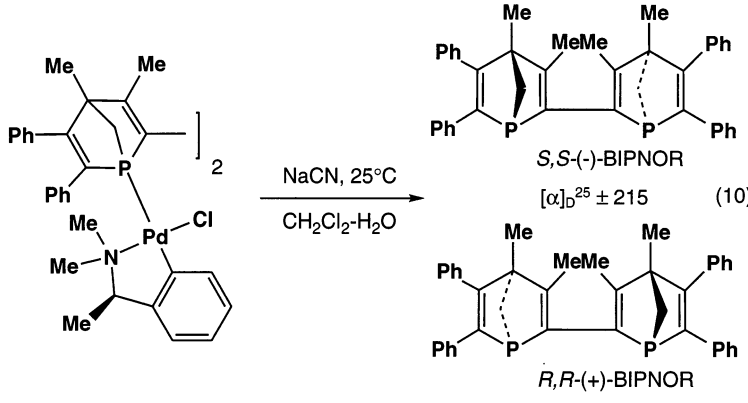
(8)

The key step of this synthesis is a double [1,5] shift of each phosphole around the other ring. The *meso* and *rac* diastereomers were separated by chromatography on silica gel as their $PdCl_2$ complexes. The resolution of the racemic mixture was carried out by coordination with an optically active palladacycle and chromatographic separation of the resulting diastereomers [17] (Eq. 9).

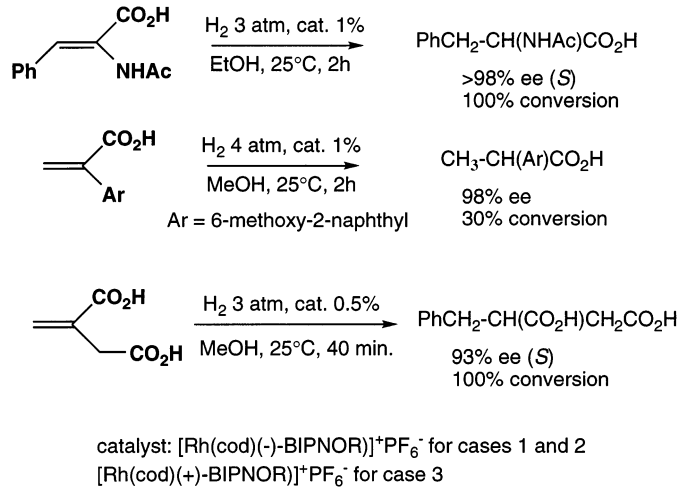


(9)

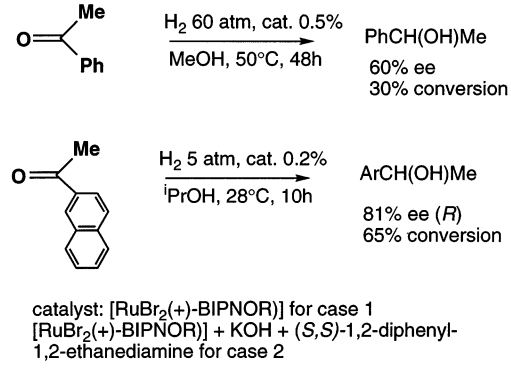
The absolute configurations were established by X-ray crystal structure analysis of one of the diastereomeric palladium complexes. The free *R*,*R* and *S*,*S*-BIPNOR were recovered from their complexes by treatment with sodium cyanide (Eq. 10).



(10)



Scheme 2. Asymmetric hydrogenation of functional alkenes with Rh(I)-BIPNOR catalysts.



Scheme 3. Asymmetric hydrogenation of ketones with Ru(II)-BIPNOR catalysts.

As cationic Rh(I) complexes, these pure enantiomers display high efficiency in the enantioselective hydrogenation of functional alkenes (Scheme 2).

The observed ee's are in the same range as those obtained with BINAP- and DuPHOS-based catalysts.

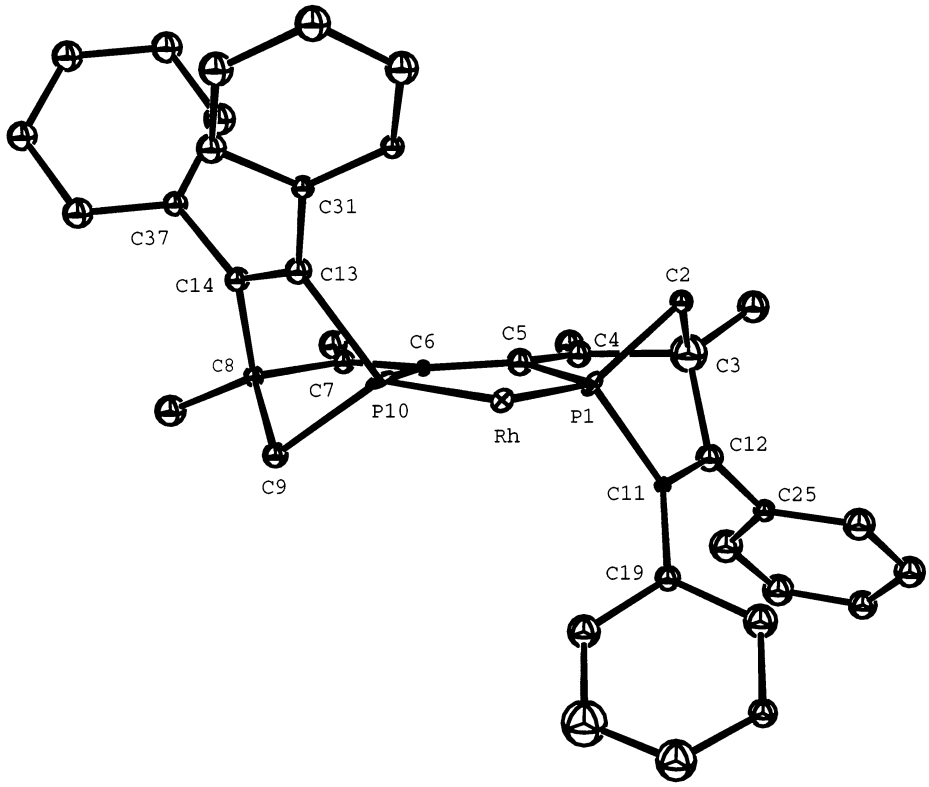


Fig. 1. View of the [Rh(−)-BIPNOR] moiety of [Rh(cod)(−)-BIPNOR]$^+PF_6^-$ from the P_1RhP_{10} plane.

As Ru(II) complexes, the enantiomers of BIPNOR appear to be less efficient than the BINAP-based catalysts in the asymmetric hydrogenation of ketones (Scheme 3), although the optimisation of the experimental conditions has not been carried out yet in that case.

It seems that the BIPNOR geometry is especially well suited to the transfer of chirality in a square–planar Rh(I) complex as shown in Fig. 1. The [Rh(−)-BIPNOR] moiety occupies two quadrants of the space around Rh and leaves the two others free. This situation induces an optimum face-selection during the complexation of the incoming prochiral alkene as discussed by Knowles [13]. More work is currently being done in order to define the scope of BIPNOR in enantioselective catalysis.

Acknowledgements

The authors thank Dr. Michel Spagnol (RP) for his help in the evaluation of the performances of BIPNOR in asymmetric catalysis. The work on BIPNOR was supported by several contracts of Rhône-Poulenc. The previous work on the chemistry of 2*H*-phospholes was supported by CNRS and Ecole Polytechnique.

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