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## Chiral *N*-phosphino sulfinamide ligands in rhodium(I)-catalyzed [2+2+2] cycloaddition reactions

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This manuscript is dedicated to Professor Carmen Nájera on the occasion of her 60th birthday

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### ABSTRACT

The combination of cationic rhodium(I) complexes with *N*-phosphino *tert*-butylsulfinamides (PNSO) ligands is efficient for catalytic intra- and intermolecular [2+2+2] cycloaddition reactions. PNSO ligands are a new class of chiral bidentate ligands, which have the characteristic of combining the easily accessible sulfur chirality with the coordinating capacity of phosphorous. Cycloaddition of open-chained and macrocyclic *E*-enediynes with these chiral complexes have proved to be highly efficient in terms of yields, giving moderate enantiomeric excesses of the corresponding cyclohexadiene derivatives. In addition Rh(I)/PNSO complexes catalyzed the intermolecular cycloaddition of diynes with monoalkynes in mild reaction conditions and short reaction times.

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### 1. Introduction

Transition-metal-catalyzed-[2+2+2] cycloadditions are valuable strategic reactions in increasing the complexity of target molecules as they enable several bond connections to be made in a single step.<sup>1</sup> This reaction is remarkable in terms of its ability to generate carbocyclic systems by the involvement of various unsaturated substrates, such as alkynes and alkenes. In addition, the enantioselective version of these [2+2+2] cycloadditions is a powerful synthetic method for the construction of chiral cyclic frameworks.<sup>1h,k</sup> Various transition metal catalysts based especially on Ni, Co, Rh, Ru, and Pd have been developed for cyclotrimerization reactions. Given the potential of the process, it is extremely interesting to search for new efficient catalytic systems, which allow us to work, for example, in mild reaction conditions or with air-stable complexes. Some of us have recently described the synthesis of a new class of chiral bidentate ligands: *N*-phosphino *tert*-butylsulfinamides (PNSO, **I**, Fig. 1). These ligands represent an efficient way of combining the easily accessible sulfur chirality with the coordinating capacity of phosphorous. Ligands **I** are modular and can

be conveniently assembled from the commercially available enantiopure *tert*-butylsulfinamide, an aldehyde, and a chlorophosphine in two steps. Some of these ligands, such as **1a** have proved to be highly efficient in the intermolecular asymmetric Pauson–Khand reaction acting as bidentate P,S ligands.<sup>2</sup> This study was the first example of a chiral sulfur atom coordinated to a cobalt center.

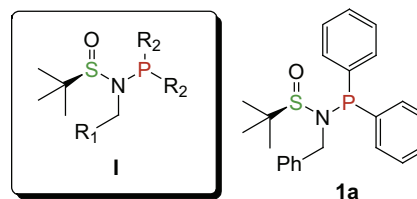


Fig. 1. General structure of the *N*-phosphino *tert*-butylsulfinamides (PNSO) chiral ligands.

We recently reported the first rhodium(I) complexes with PNSO ligands of type **I**. The reaction of [RhCl(COD)]<sub>2</sub> with 1 or 2 equiv of **1a** in the presence of 1 equiv of AgOTf, afforded complexes [Rh(**1a**)(COD)]OTf and [Rh(**1a**)<sub>2</sub>]OTf in good yields.<sup>3</sup> We observed that PNSO ligands, depending on the electronic environment around the

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