

## Sulfinylmethyl Phosphines as Chiral Ligands in the Intermolecular Pauson–Khand Reaction

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A new family of enantiomerically pure *p*-tolyl and *tert*-butyl sulfinylmethyl phosphine ligands is described. Ligands with an extra chiral center in the central carbon atom were prepared by phosphinylation of benzyl and homobenzyl sulfoxides. Ligand exchange reaction of these compounds with Co<sub>2</sub>-alkyne complexes afforded up to 6:1 dr. The resulting bridged complexes were tested in the intermolecular Pauson–Khand reaction to provide up to 97% ee.

### Introduction

Since its discovery in 1973, the ability to synthesize cyclopentenones in a straightforward way aroused interest in the Pauson–Khand reaction (PKR)<sup>1</sup> and has led to the development of new complexes and catalysts capable of performing the reaction in an enantioselective fashion.<sup>2</sup> Apart from cobalt, other metals, such as Ru,<sup>3</sup> Ir,<sup>4</sup> Ni,<sup>5</sup> or Rh,<sup>6</sup> have also been successfully used in the intramolecular version of this reaction. Currently, one of the major challenges still to be tackled is the development of an efficient catalyst for the asymmetric intermolecular version of the PKR. In our efforts to find efficient ligands for the asymmetric PKR,<sup>7</sup> we have recently reported a new family of *N*-phosphine sulfonamide (PNSO) ligands that give high yields and high ee's in the asymmetric intermolecular PKR (Figure 1).<sup>8</sup>

The main feature of these bidentate ligands is that the phosphorus atom provides metal affinity, while the sulfur moiety is the source of chirality. However, few examples of phosphorus-sulfoxide bidentate ligands have been described in the literature.<sup>9,10</sup> One of the few examples of phosphorus-sulfoxide bidentate ligands described is the *p*-tolylsulfinylmethyl phosphine **1** (Figure 1). When pure, compound **1** is stable toward oxygen migration, although it can be prepared in only 23% yield.<sup>11</sup>

Considering the success achieved with the use of PNSO ligands in the asymmetric intermolecular PKR, we thought it important to study the effect of changing the central nitrogen for a carbon atom and the introduction of an extra chiral center in the ligand. Thus, here we describe the synthesis of a family of ligands of general formula **III** (PCSO ligands), their coordination behavior toward alkyne-dicobalt complexes, and the intermolecular asymmetric PKR of the resulting complexes.

### Results and Discussion

The general strategy for the preparation of PCSO ligands was the reaction of the corresponding  $\alpha$ -sulfinyl carbanions with Ph<sub>2</sub>PCl (Scheme 1). Thus, ligand **1** was prepared by alkylation of commercially available (*R*)-*p*-tolyl methyl sulfoxide (**2**) with chlorodiphenyl phosphine at –78 °C, followed by protection *in situ* with borane to prevent oxygen migration. Using this strategy, the yield of compound **1**-BH<sub>3</sub> was improved from 23% to 43%.

For the preparation of PCSO ligands bearing an additional chiral center on the central carbon atom, benzyl and homobenzyl sulfoxides **3** and **5** were used as starting

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