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Note

Synthesis of chiral nonracemic PC(sp^3)P pincer ligands

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ABSTRACT

The manuscript describes a straightforward synthetic route toward a new family of chiral nonracemic dibenzobarrelene-based pincer ligands. The target molecules have been synthesized via lithiation of the racemic 1-bromo-8-diphenylphosphinotriptycene (2) and subsequent quenching with diastereomerically pure (1R,2S,5R)-(−)-menthyl (*S*)-*p*-toluenesulfinate. The resulting mixture of diastereomers was resolved using conventional column chromatography. Hydrogenation of the diastereomerically pure compounds lead to the formation of enantiopure PCS ligands.

1. Introduction

Pincer-like compounds, bearing meridionally coordinating tridentate ligands, are now well-studied and recognized as efficient catalysts in a variety of chemical transformations [1]. However, unlike other ligands' families, most of known chiral pincer-type systems perform only moderately as catalysts in enantioselective reactions [2]. One of the possible reasons to a somewhat disappointing catalytic activity of the otherwise powerful compounds may be their structural simplicity.

Indeed, with regard to the carbometalated pincer complexes, the vast majority of reported substances possess a sp^2-hybridized carbon. They, with some exceptions of C_2-symmetrically twisted molecules, are averagely planar (Fig. 1) [3].

Unlike those, a more efficient substrate orientation leading to more efficient enantiocontrol may be achieved by more complex and three-dimensional environment around the metal center in C(sp^3)-based pincer ligands. Unfortunately, such compounds appear in the literature only occasionally (Fig. 2) [4].

Some time ago our group introduced a new dibenzobarrelene-based scaffold, as a platform for the construction of sp^3-carbometalated complexes (Fig. 3) [5]. Synthesis of the ligands and their complexes is very modular as it relies on a straightforward and robust Diels–Alder cycloaddition strategy [6]. The new pincer complexes proved themselves as highly active catalysts for the transfer hydrogenation of ketones, as well as transfer and acceptorless dehydrogenative coupling of alcohols [7].

Considering a general interest to the synthesis of more structurally complex chiral pincer ligands and a beneficial activity of dibenzobarrelene-based ligands in chemical transformations for which the development of enantioselective version is of great interest, in particular, we decided to invest efforts into the synthesis of chiral enantiopure ligands of this type.

2. Results and discussion

The synthesis of chiral nonracemic triptycene-based ligands is shown in Scheme 1. The synthesis starts with the preparation of a racemic 1-bromo-8-diphenylphosphinotriptycene (**2**) from the readily accessible 1,8-dibromotriptycene (**1**) that can be prepared from commercially available starting materials on 50 g-scale [8]. The monophosphine derivative **2** forms via a selective monolithiation of **1** with *n*-BuLi/TMEDA complex in THF and subsequent quenching with chlorodiphenylphosphine. Noteworthy, the monolithiation takes place smoothly and results in the formation of the ca. 95% pure intermediate. An additional *n*-BuLi treatment followed by quenching with diastereomerically pure (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-*p*-toluenesulfinate leads to the mixture of the diastereomers **3** and **3′** in acceptable yield.

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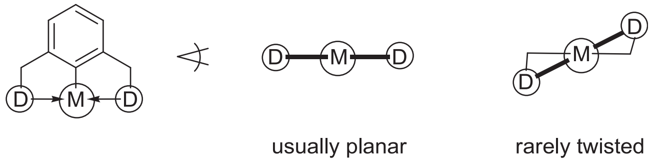


Fig. 1. Dimensionality of PC(sp^2)P pincer complexes.

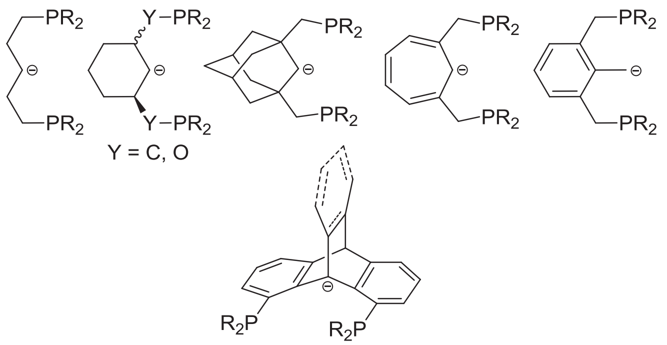


Fig. 2. PC(sp^3)P ligands known in the literature (top) and PC(sp^3)P ligands developed by our group (bottom).

Careful column chromatography on silica gel using 10% ethyl acetate/hexane provides the diastereomers in ca. 20% yield each.

^{31}P NMR shows expectedly different signals for each diastereomer that appear at −14.3 and −15.2 ppm. The absolute configuration was determined after structural characterization of the single crystal of **3** (flack parameter calculated for the enantiomeric crystal structure was 0.06). Fig. 3 (left) represents the ORTEP drawing for **3** (*9S,10S*).

At the next stage, we attempted to prepare chiral nonracemic diphosphine **6** via replacement of the chiral sulfur oxide group with a phosphine bearing different substituents by lithiation/chlorodialkylphosphine treatment. Unfortunately, lithiation of the diastereomerically pure **3** or **3′** yielded mainly non-chiral diphenyl phosphinotriptycene **7** accompanied with only traces of the desired diphosphine **6**. The desulfurization of **3** or **3′** occurs, apparently, due to equilibrium being established between the intermediates **4**–**5** and **7**–**8** that favors the neighboring group-stabilized **8** (Scheme 2).

It was found that low isolated yields of the diastereomerically pure **3** and **3′** are due to their relatively high sensitivity towards oxygen during column chromatography. Thus, we checked a

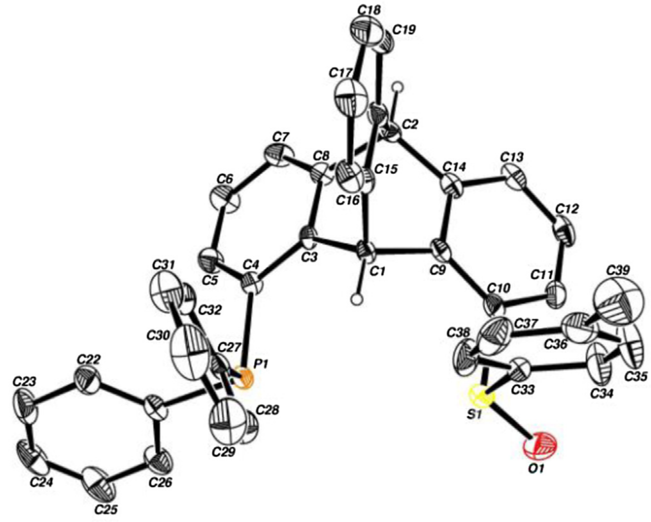
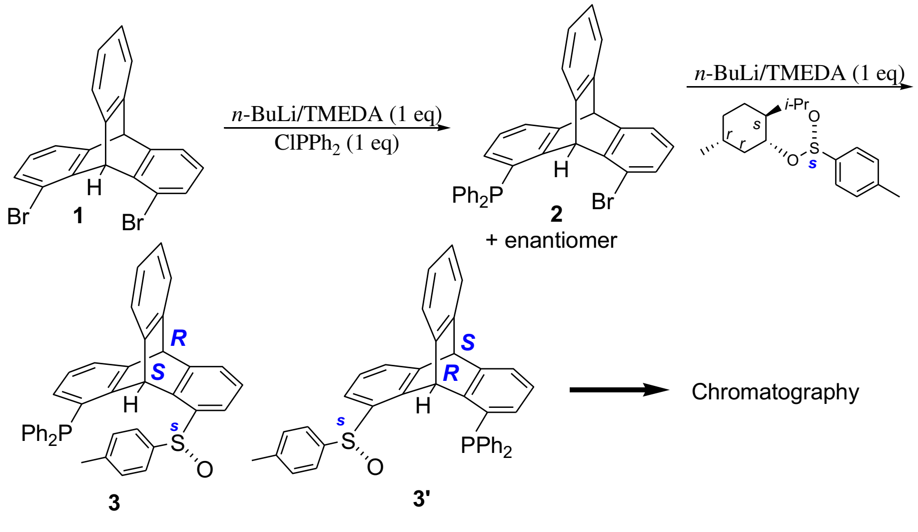


Fig. 3. ORTEP drawing (50% probability ellipsoids) of **3**. Hydrogen atoms and solvent molecules are omitted for clarity.



Scheme 1. Synthesis of **3** and **3′**.