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A study on the optical resolution of 1-isopropyl-3-methyl-3-phospholene 1-oxide and its use in the synthesis of borane and platinum complexes

Péter Bagi [a], Kinga Juhász [a], István Timári [b], Katalin E. Kövér [b], Dávid Mester [c, d], Mihály Kállay [c, d], Miklós Kubinyi [d, e], Tibor Szilvási [f], Péter Pongrácz [g], László Kollár [g], Konstantin Karaghiosoff [h], Mátyás Czugler [a], László Drahos [e], Elemér Fogassy [a], György Keglevich [a, *]

[a] Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, 1521 Budapest, Hungary
[b] Department of Inorganic and Analytical Chemistry, University of Debrecen, 4032 Debrecen, Hungary
[c] MTA-BME Lendület Quantum Chemistry Research Group, Budapest University of Technology and Economics, 1521 Budapest, Hungary
[d] Department of Physical Chemistry and Material Science, Budapest University of Technology and Economics, 1521 Budapest, Hungary
[e] Research Centre for Natural Sciences, Hungarian Academy of Sciences, 1525 Budapest, Hungary
[f] Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, 1521 Budapest, Hungary
[g] Department of Inorganic Chemistry, University of Pécs and Szentágothai Research Center, 7624 Pécs, Hungary
[h] Department Chemie und Biochemie, Ludwig-Maximilians-Universität München, 81377 München, Germany

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ABSTRACT

A 1-isopropyl-3-phospholene 1-oxide was prepared and the two enantiomers were isolated from the racemate by resolution using optically active TADDOL derivatives or the acidic Ca^{2+} salts of (−)-*O*,*O*-diaroyl-(2*R*,3*R*)-tartaric acids. The single crystal X-ray structure of the 1-isopropyl-3-phospholene oxide − spiro-TADDOL 1:2 associate revealed the mode of binding between the host and guest molecules. The role of the interactions between the three molecules was supported not only by the contact data, but also force field and semiempirical calculations. Beside X-ray analysis, the absolute configuration of the P-stereogenic center was also determined on the basis of CD spectroscopy and high level quantum chemical calculations. The racemic and optically active 1-isopropyl-3-phospholenes obtained after deoxygenation were converted to the corresponding borane complexes and Pt(II) complexes. Stereostructure of the latter species was evaluated by high level quantum chemical calculations and the Pt complexes were tested as catalysts in the hydroformylation of styrene.

1. Introduction

The transition metal phosphine complexes are widely used catalysts in homogenous catalytic reactions, such as hydrogenation and hydroformylation that underlines the importance of phosphines among organophosphorus compounds [1,2]. Among the phosphine ligands, the P-stereogenic P(III)-compounds are of great importance. The P-heterocyclic derivatives form a special group [3]. However, there are only a few examples in the literature for P-heterocyclic phosphines bearing an asymmetric phosphorus atom [4–6].

Although an increasing number of examples can be found in the literature for the asymmetric syntheses of P-stereogenic compounds [7–9], in most cases the resolution of the corresponding racemic compounds is the method of choice for the preparation of optically active organophosphorus compounds including P-heterocyclic derivatives with a P-stereogenic center [6,10]. Many examples can be found in the literature for the resolution of cyclic P-chiral phosphines, phosphine oxides and phosphonium salts via the formation of covalent diasteromers [11–13], diastereomeric coordination [14–19], molecular complexes [10,20,21] or diastereomeric salts [22–27].

In the literature, the synthesis of a few optically active P-chiral heterocyclic ligands was described and the transition metal complexes of these P(III)-compounds were used as catalysts mainly

* Corresponding author.
E-mail address: gkeglevich@mail.bme.hu (G. Keglevich).

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in enantioselective hydrogenation reactions [11,13,16,18,21,28–32]. There are only a few examples for P-heterocyclic ligands that were used in hydroformylation [5]. Among the transition metal phosphine complexes that can be used as catalyst in hydroformylation, the platinum complexes of P-heterocycles form a class that needs further investigations. Prigle et al. reported the synthesis of the platinum complexes of several 5-, 6- and 7-membered P-heterocycles [33,34]. Gouygou et al. synthesized a few bisphosphole platinum-complexes [35]. Recently, our research group contributed to the research of optically active P-stereogenic phosphine oxides, as well as to the synthesis of platinum-complexes incorporating P-chiral heterocyclic ligands. TADDOL-derivatives and the Ca^{2+} salts of dibenzoyl- and di-*p*-toluoyl-tartaric acid were applied as the resolving agents to prepare the enantiomers of the aryl- and alkyl-3-phospholene oxides [36–42], as well as a few six-membered P-heterocyclic phosphine oxides, embracing a 1,2-dihydrophosphinine oxide and a 1,2,3,6-tetrahydrophosphinine oxide [43,44]. We have also reported the synthesis of a few racemic and optically active borane and platinum-complexes bearing aryl- and alkyl-3-phospholene ligands. The 3-phospholene - platinum complexes were applied as catalysts in the asymmetric hydroformylation of styrene and enantioselectivities up to 29% were obtained [45–48].

As a continuation of this ongoing research, we wished to proceed with our systematic investigation of the resolution of the 3-phospholene oxides. Another aim of ours was to gain a deeper understanding how the substituents of the 3-phospholene moiety influence the catalytic activity of the platinum-complexes incorporating 3-phospholene ligands. In this paper, we report the synthesis and the resolution of the 1-isopropyl-3-methyl-3-phospholene oxide. The 1-isopropyl-3-methyl-3-phospholene-borane and platinum complexes were also prepared in racemic and optically active forms, and the platinum-complexes were tested as catalysts in the hydroformylation of styrene.

2. Results and discussion

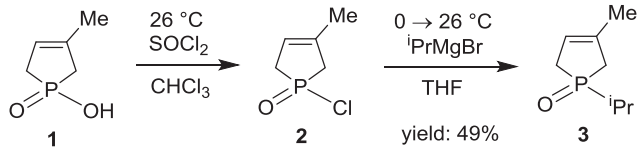
2.1. Synthesis and resolution of 1-isopropyl-3-methyl-3-phospholene 1-oxide (3)

1-Isopropyl-3-methyl-3-phospholene 1-oxide (**3**) was prepared by extending the synthetic method elaborated for other alkyl- and aryl-3-methyl-3-phospholene oxides [37,47,49]. 1-Hydroxy-3-methyl-3-phospholene 1-oxide (**1**) was reacted with thionyl chloride to form the corresponding phosphinic chloride (**2**) which was immediately reacted with isopropylmagnesium bromide to afford 1-isopropyl-3-methyl-3-phospholene 1-oxide (**3**) in a yield of 49% (Scheme 1). As a new compound, the isopropyl-phospholene oxide (**3**) was characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, as well as HRMS.

To prepare the enantiomers of isopropyl-phospholene oxide (**3**), the resolution of racemic phosphine oxide **3** was first attempted with TADDOL-derivatives [(−)-**4** and (−)-**5**] that were found to be efficient resolving agents for other aryl- and alkyl-3-phospholene oxides [36,37,40].

A few resolution experiments of isopropyl-phospholene oxide (**3**) with TADDOL-derivatives [(−)-**4** and (−)-**5**] were carried out in a mixture of ethyl acetate and hexane. In these cases, the mixture of the racemic compound (**3**) and the given resolving agent [(−)-**4** or (−)-**5**] was dissolved in hot ethyl acetate, and the corresponding diastereomer precipitated on adding hexane to the reaction mixture.

Applying alcohols, such as methanol, ethanol or isopropanol as the solvent, the racemic compound (**3**) and the resolving agent [(−)-**4** or (−)-**5**] were dissolved in hot alcohols, and the diastereomer appeared by gradually cooling down the reaction mixture to 26 °C (Scheme 2).



Scheme 1.

In all instances, the corresponding diastereomers were separated from the mother liquor by filtration after 3 h of crystallization, and they were purified further by two recrystallizations. The composition of the corresponding diastereomers was established by ^{1}H NMR spectroscopy. The enantiomeric mixture of isopropyl-phospholene oxide (**3**) was recovered from the given diastereomer by column chromatography using silica gel and a 97:3 mixture of dichloromethane and methanol as the eluent. The enantiomeric excess of the isopropyl-phospholene oxide (**3**) was analysed by chiral GC.

The results leading to enantiomeric separation of the target molecule **3** were summarized in Table 1. Beside the yield and the enantiomeric excess, the resolving capability (S) was also determined. The resolving capability (S) is used to describe the overall efficiency of a given resolution and this value can be calculated as the product of the yield and the enantiomeric excess.

Applying TADDOL [(−)-**4**] as the resolving agent for the enantiomeric separation of 3-phospholene oxide **3**, the crystalline diastereomers were obtained in the cases, when ethyl acetate/hexane or isopropyl alcohol was used (Table 1, Entries 1 and 2). However, the enantiomeric discrimination between the two antipodes of 1-isopropyl-3-phospholene oxide (**3**) was poor in these instances, as the highest enantiomeric excess and resolving capability values were 6% and 0.05, respectively (Table 1, Entry 1). It is noteworthy that no diastereomeric complex was obtained when methanol or ethanol was used as the solvent, and the TADDOL [(−)-**4**] precipitated exclusively in these instances.

Applying spiro-TADDOL [(−)-**5**] as the resolving agent, the enantiomeric excess and the resolving capability values were solvent dependent, and the ee was between 57 and 95%, and the resolving capability fell in the range of 0.34–0.47 (Table 1, Entries 3–6). It is noteworthy that the solvent also influenced which isopropyl-phospholene oxide (**3**) enantiomer was incorporated into the corresponding diastereomer. (+)-(*R*)-1-Isopropyl-3-phospholene oxide [(+)-**3**] could be prepared with spiro-TADDOL [(−)-**5**] in ethyl acetate/hexane or methanol (Table 1, Entries 3 and 4). Carrying out the resolution in ethanol or in isopropyl alcohol led to the other (−)-(*S*)-1-isopropyl-3-phospholene oxide antipode [(−)-**3**] (Table 1, Entries 5 and 6). Moreover, the solvent also affected the composition of the diastereomers. A diastereomeric complex incorporating isopropyl-phospholene oxide (**3**) and spiro-TADDOL [(−)-**5**] in a 1:1 ratio was obtained in ethyl acetate/hexane and isopropyl alcohol (Table 1, Entries 3 and 6), and the diastereomer having the composition of (**3**)·(spiro-TADDOL)$_2$ was separated when methanol or ethanol was used as the solvent (Table 1, Entries 4 and 5).

These results indicated that the TADDOL analogue (−)-**5** could be used more efficiently for the enantiomeric separation of phosphine oxide **3,** than the TADDOL [(−)-**4**] itself (compare Table 1, Entries 1–2 and 3–6).

The observation that both isopropyl-phospholene oxide antipodes [(+)- and (−)-**3**] could be prepared with the same resolving agent, (spiro-TADDOL [(−)-**5**]) in different solvents allowed us to develop a procedure for the preparation of the (+)- and