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Chiral [2.2]paracyclophane-based NAC- and NHC-gold(I) complexes

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Dedicated to Prof. Hubert Schmidbaur on the occasion of his 80th birthday.

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ABSTRACT

From enantiomerically pure, planar chiral [2.2]paracyclophane amines a series of nitrogen acyclic carbenegold(I) complexes and nitrogen heterocyclic carbenegold(I) complexes are prepared by a modular template synthesis using isonitriles and amines. These chiral catalysts are tested in two reactions, the enantiotopos-selective furanyne cyclization and the enantioselective enyne cyclization. While excellent conversions could be achieved with these new catalysts, the enantioselectivities in only some cases are in the range of best known catalysts for these conversion.

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Introduction

In both the inorganic and the organometallic chemistry of gold the ligands play a pivotal role [1,2]. Metal complexes containing paracyclophanes (PCPs) as ligands are already known [3–6]. Their application as chiral catalysts is of significant interest as they possess planar chirality. Gold complexes based on PCP were first prepared in situ in 2011 by Michelet et al. [7]. These complexes were used for the domino cyclization/nucleophile addition reactions of enynes in the presence of water, methanol, or electron-rich aromatic derivatives, but the results concerning this reaction using the famous PhanePhos ligand were unsatisfactory. In 2012, however, Gagné published a gold-catalyzed Cope rearrangement where the highest yield and enantiomeric excess were found for the PhanePhos ligand [8]. Both these innovative first investigations in homogeneous gold catalysis were conducted with PCP-phosphane ligands. So far, only silver and rhodium NHC complexes with PCP substructure have been reported [9], until now there exist no *N*-hetereocyclic carbenegold complexes containing a PCP substituent.

We now report the synthesis and application of the first PCP-based NAC and NHC gold complexes.

Results and discussion

Synthesis and characterization

The starting material for the synthesis of the new gold(I) complexes was the PCP-amine **4**, which was conveniently prepared in enantiomerically pure form from the achiral PCP **1** in three steps by published methods (Scheme 1) [10]: a simple electrophilic aromatic substitution provided the bromo-PCP **2**, which then was transferred into the azide **3** with *n*-BuLi and tosylazide. A reduction with sodiumborohydride delivered racemic **4**, whose enantiomers were separated via HPLC on a CHIRALPAK IB column using *n*-hexane/Isopropanol (75/25). The retention times on the analytical

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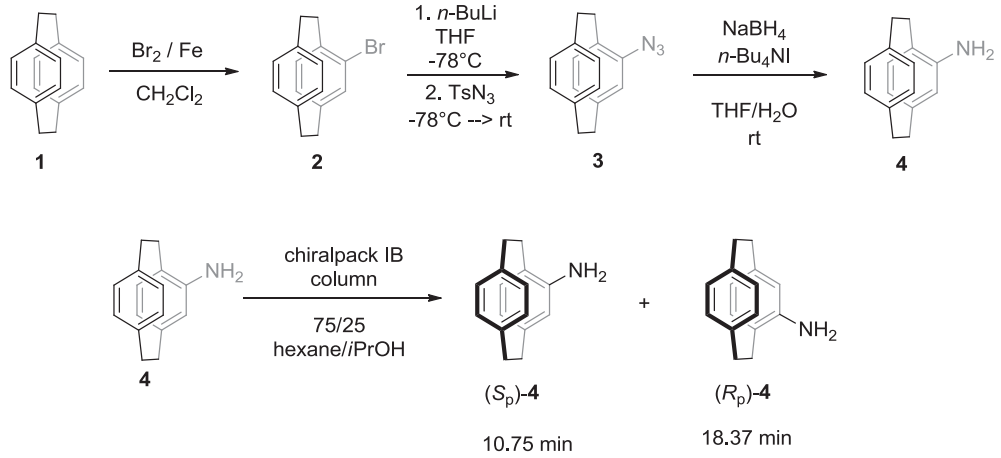

Scheme 1. Synthesis of the enantiomerically pure amine **4**.

column were 10.75 min for the (+)-enantiomer and 18.37 min for the (−)-enantiomer. The absolute configuration of the first eluting (+)-enantiomer could then be assigned via X-ray diffraction of the corresponding hydrochloride (Fig. 1) by analysis of the Flack parameter (absolute structure parameter X = 0.04(9)) [11].

The enantiomerically pure amine then was converted into the isonitrile. The reaction of **4** with ethyl formate at reflux temperature delivered the formamide **5**, which was purified by recrystallization from acetone/pentane. **5** delivered the isonitrile (S_p)-**6** when treated with phosphorylchloride and triethylamine in THF (Scheme 2).

Finally, the synthesis of the nitrogen acyclic carbene (NAC) complex [12] was achieved by reacting the simple (Me_2S)gold(I) chloride, isonitrile (S_p)-**6**, and a secondary amine which directly lead to the desired gold complex (S_p)-**7** in an excellent yield (Scheme 3).

Different amines were tested in combination with (S_p)-**6** in order to demonstrate the broad scope of this methodology. Apart from two achiral amines, which led to the enantiomerically pure NAC-gold(I) complexes (S_p)-**8** and (S_p)-**9**, also enantiomerically pure amines were used. The latter provided NAC ligands which combined planar and central chirality on each side of the NAC. Thus, both diastereomers of **10** and complex **11** were obtained in good yields. The excess of amine had to be removed by several washings with hexane and recrystallization from DCM/hexane, which reduced the yields shown in Fig. 2.

For **11** a suitable crystal for a single crystal X-ray structure analysis could be grown. The structure of the complex is shown in Fig. 3 [11], it confirmed the absolute configuration of the

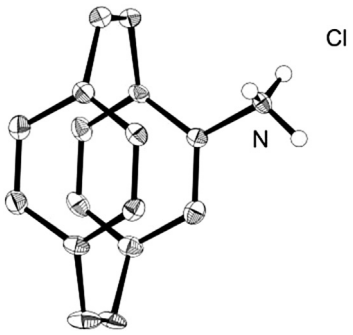

Fig. 1. Solid state molecular structure of (S_p)-**4**.

paracyclophane unit and the bis(phenylethyl) amine moiety. As expected, the steric bulk of the chiral (*S*,*S*)-bisphenylethyl amine moiety positions the PCP group *syn* to the gold centre on the carbene ligand. However, the low quality of the results doesn't allow a detailed discussion. Hence, we take the results only as a proof of constitution and configuration.

In addition to NAC-gold(I) complexes we also wanted to prepare NHC-gold(I) complexes. This was achieved by employing the functionalized amine building block **12** [13]. This amine gave the NAC complex (Sp)-**13** upon addition of the in situ-generated isonitrilegold(I) chloride. The NAC ligand in the gold complex could then be cyclized to the unsaturated NHC ligand bound to the gold centre by a condensation and elimination reaction treatment initiated by acid. In this way we were able to obtain the complexes (S_p)-**15** and (S_p)-**16**, the first one in low, the second one in high yield (Scheme 4).

Synthesis of chiral gold(I) complexes without PCP ligands

In order to evaluate the influence of the PCP ligands on the catalyst performance of the gold complexes we also prepared some other chiral gold complexes that lack the PCP moiety as reference catalysts: First (*R*)-**17** (Fig. 4) was prepared according to the usual method for the synthesis of NAC-gold(I) complexes.

As demonstrated by Gagné et al. [8], the dinuclear PCP-substituted gold complex delivers the best enantiomeric excess in Cope rearrangements. Thus, another target was the synthesis of a dinuclear NAC gold complex. From binaphtyldiamine the bis(isonitrile) was prepared by following the route described above. Subsequently, with di-*n*-propylamine and (Me_2S)gold(I) chloride the complex (S_a)-**18** was obtained in a good yield of 79% (Fig. 5).

As the corresponding chiral PCP-diamine was not available, it was not possible to prepare a dinuclear PCP-substituted NAC-gold(I) complex analogue in optically pure form.

Catalytic reactions

For the investigation of the catalytic activity in enantioselective reactions two test reactions were selected. The first one is the asymmetric phenol synthesis, which has already shown to give some enantiomeric excess with phosphane ligands [14]. However, so far chiral carbene complexes have not been tested in this reaction. The substrate for this test reaction was prepared by following a previously described route [14]. Deprotonation of the 2-

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