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Benzazaphospholine-2-carboxylic acids: Synthesis, structure and properties of heterocyclic phosphanyl amino acids

Mohammed Ghalib [a], Joanna Lach [a], Olga S. Fomina [a,b], Dmitry G. Yakhvarov [b,c], Peter G. Jones [d], Joachim Heinicke [a,*]

[a] Institut für Biochemie (Anorganische Chemie), Ernst-Moritz-Arndt-Universität Greifswald, Felix-Hausdorff-Str. 4, 17487 Greifswald, Germany
[b] A.E. Arbuzov Institute of Organic and Physical Chemistry, Arbuzov str. 8, 420088 Kazan, Russian Federation
[c] Kazan (Volga Region) Federal University, Kremlevskaya str. 18, 420008 Kazan, Russian Federation
[d] Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

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ABSTRACT

1,3-Dialkyl-1,3-benzazaphospholine-2-carboxylic acids **2a**,**b** can be conveniently prepared by metalation and alkylation of *N*-methyl- and *N*-neopentyl-*o*-phosphanylaniline in liquid ammonia and cyclocondensation of the resulting *N*,*P*-disecondary phosphanylanilines **1a**,**b** with glyoxylic acid hydrate (GAH) in ether. The primary neopentylphosphanylaniline reacts with two equivalents of GAH and forms a phosphanyl-bis(amino acid) **3** with toluidine. α-Branched *P*-substituents induce strongly preferred formation of *trans*-diastereoisomers with *R*,*R*- and *S*,*S*-configuration at P and C2, as shown by a crystal structure analysis of **2a**, whereas a *P*-neopentyl (*P*-Np) group gives rise to *trans*/*cis*-diastereoisomeric mixtures. The *trans*-configuration exhibits the P lone-pair in *cis*-position to the COOH group, suitable for formation of five-membered chelate rings, as in diphenylphosphanylacetate nickel catalysts for ethylene oligomerization. Screening of **2a**,**b**/Ni(COD)$_2$ solutions in THF by a batch procedure indeed showed formation of catalysts for conversion of ethylene to linear oligomers and waxy low-molecular weight polymers. The conversion depends strongly on the size of the *N*-alkyl group, being slow and limited for the *N*-Me catalyst **2a**/**Ni** and much faster and more complete for the *N*-Np-substituted catalysts **2b**/**Ni** and **2c**/**Ni** (*N*-Np, *P*-*t*Bu). Comparison of **2b**/**Ni** with **2c**/**Ni** shows that the more bulky P-substituent further increases the catalyst activity.

1. Introduction

Recent studies on the synthesis of bulky *tert*-butyl-substituted heterocyclic phosphane ligands by addition of *tert*-butyllithium at the P=C bond of aromatic phosphorus heterocycles have included the discovery of a convenient route to 3-*tert*-butyl-1,3-benzazaphospholine-2-carboxylic acids [1]. These possess the same P-C-COOH structural unit as diphenylphosphanylacetic acid [2], which is used in the generation of nickel catalysts for the ethylene oligomerization in the SHOProcess [3], and also form highly active catalysts for this reaction. The amino function did not interfere with the catalytic conversion. This was observed also for various acyclic alkylamino- and arylamino-diphenylphosphanyl-acetic acids (phosphanylglycines) [4], whereas more closely related heterocyclic 3-phenyl-1,3-azaphospholidine-2-carboxylic acids (3-phenyl-phosphaprolines) without benzo-annulation required activation by sodium hydride to form active catalysts with Ni(COD)$_2$ [5]. To find out whether the higher activity of the benzazaphospholine-2-carboxylate-based nickel catalysts is attributable to the bulky *P*-*tert*-butyl substituent or to electronic effects of the intrinsic *o*-aminophenyl group, a preliminary study of the synthesis of less bulky *P*-alkyl-1,3-benzazaphospholine-2-carboxylic acids and their performance as ligands in the nickel catalyzed ethylene oligomerization was carried out.

2. Results and discussion

A well established strategy was chosen for the synthesis, namely the cyclocondensation of 2-phosphanyl-substituted amines, long since known for simple aldehydes and ketones [6]. Even the reaction of *o*-phosphanylaniline with pyruvic acid was reported to give 2-methyl-1,3-benzazaphospholine-2-carboxylic acid, but information on the properties and structure of this compound, except for the detection of a P–H absorption in the range 2240–2280 cm^{-1}, is not available [6c]. We used the condensation with glyoxylic acid hydrate (GAH). This acid proved sufficiently reactive at room temperature to undergo autocatalyzed

* Corresponding author. Tel.: +49 864318; fax: +49 3834 864377.
E-mail address: heinicke@uni-greifswald.de (J. Heinicke).

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