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Functionalized phosphorus derivatives of Salpen-like compounds: Synthesis and preliminary complexation studies

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Abstract

A new class of Salpen analogues based on phosphorus derivatives where the classical alkylene backbone has been replaced by a N–P–N linkage is described. Such linkage both affords a very good stability in water and an additional (fifth) potentially complexing site. The classical *ortho*-OH groups have been also replaced by various *ortho*-substituents, including diphenylphosphino groups. The synthesis of these compounds is easy and their structure can be varied at will at several levels. Several ways of synthesis can be used to combine the various fragments constituting these Salpen analogues. The structure of one of these fragments, an azide, was determined by X-ray crystallography. A preliminary study of the complexation ability of some of these new ligands was carried out with groups 10 (Ni) and 11 (Au) elements. Depending on the type of substituents and the type of metals used, these compounds can act as mono-, or tetra-dentate ligands.

Keywords: Salpen; Phosphorus; Hydrazone; Phosphorhydrazide; Complexation

1. Introduction

The extraordinary simplicity of the reaction of diamines with salicylaldehyde gave rise to a tremendous amount of work dedicated to the synthesis and study of complexation properties of the corresponding diimine derivatives, the so-called Salen compounds [1]. Indeed, the presence of two covalent and two coordinating sites in these ligands lead in most cases to planar complexes of transition metals, in which two free axial sites on the metal are available, which are particularly useful for catalytic experiments [2–4]. In contrast to the diimine derivatives, the analogous dihydrazone derivatives are relatively rare, despite the known better stability toward hydrolysis of hydrazones compared to imines. Dihydrazides of phosphorus constitute a variety of dihydrazine derivatives which are easily available and react readily with benzaldehydes. In particular we [5,6] and others [7] have shown that the reaction of phosphorus dihydrazides with salicylaldehyde affords the expected Salpen analogues, in which the traditional C–C–C linkage between both imines is replaced by a N–P–N linkage. Beside the complexation ability of the OH and N=CH group, well-known for Salpen derivatives, the presence of phosphorus should bring new complexation properties, using either the lone pair of phosphorus for phosphines derivatives, or the lone pairs of oxygen or sulfur for phosphoryl and thiophosphoryl derivatives. We have already shown that the complexation ability of a P=S group is enhanced when it is included in a P=N–P=S linkage [8], therefore we introduced such linkage in all the compounds we prepared in this paper. Furthermore, salicylaldehyde can be easily replaced by other *ortho*-functionalized benzaldehydes (Fig. 1). In this paper, we

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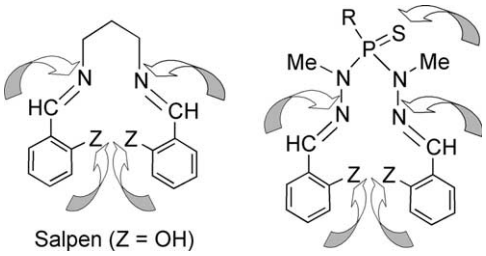


Fig. 1. Potential complexation sites in Salpen and phosphorus Salpen analogues (P-Salpen).

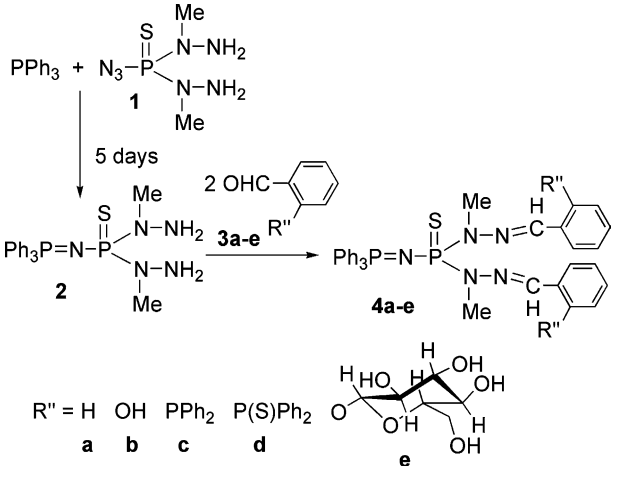
report the synthesis of a number of new phosphorus derivatives of Salpen analogues (P-Salpen), having N–PR(S)–N linkages (R = $R'_3P{=}N$), and preliminary experiments concerning the complexation properties of some of these compounds.

2. Results and discussion

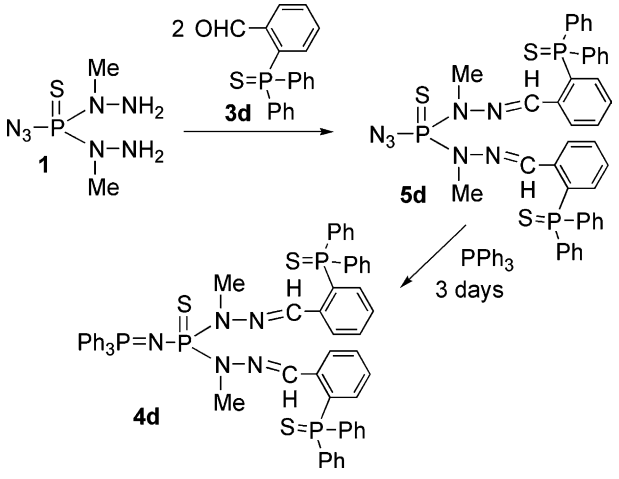
The synthesis of the phosphorus Salpen analogues necessitates first the synthesis of phosphodihydrazides $RP(S)(NMeNH_2)_2$ [9], to be used instead of 1,3-diamines. The P=N–P=S linkage is easily obtained using the Staudinger reaction [10] between a phosphine and a thiophosphoryl azide, thus the R substituent must be N_3. The reaction of triphenylphosphine with the azide **1** [11] affords slowly but cleanly the dihydrazide **2** (Scheme 1). The slowness of the reaction (5 days at room temperature) can be ascribed to the absence of strong electron-withdrawing groups on the azide, the PS group being not sufficient [12]. Compound **2** is characterized in ^{31}P NMR by a set of two doublets for the P=N–P=S linkage at $\delta = 12.4$ and 71.0 ppm, respectively, with $^2J_{PP} = 16.7$ Hz.

The next step for obtaining the Salpen analogues **4a–e** consists in the condensation of both NH_2 groups of **2** with benzaldehyde **3a** and various *ortho*-functionalized benzaldehydes: hydroxybenzaldehyde **3b**, diphenylphosphinobenzaldehyde **3c**, diphenylthiophosphino benzaldehyde **3d**, and helicin **3e** (Scheme 1). In all cases, the condensation induces a shielding of the signal corresponding to the P=S group in ^{31}P NMR from 71.0 to ca. 56 ppm, as well as a shielding in ^{13}C NMR of the doublet corresponding to the Me groups from 39.1 ppm to ca. 31 ppm. In all cases excepted for **4e**, the condensation affords a single isomer for the C=N bonds, presumably the *E* isomer in view of the X-ray structure of compound **5d** (see later). However, the ^{13}C NMR spectrum of compound **4e** displays two signals instead of one for several atoms, approximately in a 1/4 ratio. This splitting is easily detectable on the NMe groups and on several atoms of the helicin function, and the signal of the CH=N group is broadened. These data are indicative of the presence of two isomers for the CH=N groups (*E* and *Z*). We have already observed the same phenomenon for helicin linked to the surface of dendrimers [6]. Due to the presence of two β-D-glucoside groups, compound **4e** is fairly soluble in water/THF mixtures (v/v); this allowed us to test the stability of this compound. No trace of decomposition is observed even after several weeks in this mixture, illustrating the very good stability toward hydrolysis induced by the phosphorhydrazone linkages compared to imines in classical Salpen [9,13].

This method of synthesis is very simple, adaptable, and each component can be varied. For instance, both steps can be inverted, as shown by the condensation of **1** with **3d** leading to the azide **5d** (Scheme 2). In view of the small number of compounds possessing a λ^4,σ^5-phosphorus azide linkage characterized by X-ray diffraction (only five examples) [14–18], it appeared interesting to obtain single crystals of **5d**. The ORTEP drawing of **5d** is shown in Fig. 2. The X-ray structure determination (Table 1) gives a N6–N7 bond length value of 1.121(5) Å (Table 2), one of the shortest reported up to now for a λ^4,σ^5-phosphorus azide linkage, close to the value of 1.098 Å known for a triple bond [19]. The N5–N6 bond length (1.228(5) Å) is significantly shorter than a single bond, for instance when compared with



Scheme 1.



Scheme 2.