



Monoanionic salicylaldimine ligands with (thio)phosphoryl pendant arms: Synthesis and complexing features



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ABSTRACT

Schiff base condensation of *o*-(thio)phosphorylated anilines with salicylaldehyde affords novel salicylaldimine ligands **1a,b** with (thio)phosphoryl pendant arms. Under base-induced deprotonation, **1a,b** readily form complexes with Re(I) (**2a,b**), Pd(II) (**3a,b**), and Ni(II) (**4**) ions, featuring κ^2 -*N,O* (**3a**) or κ^3 -*X,N,O* (*X* = O, S) (in the other cases) coordination mode depending on the nature of the substituent *X* in the P = *X* moiety. In the absence of a base, the interaction of **1b** with (PhCN)₂PdCl₂ yields molecular complex **5** which can be readily transformed into **3b** under action of triethylamine. Moreover, complex **3b** with the deprotonated form of the ligand can be also readily synthesized by the template assembling of the corresponding aniline and salicylaldehyde on the Pd(II) ion in the presence of Et₃N. All the complexes are characterized by spectroscopic techniques (NMR, IR, and Raman) and in some cases by X-ray diffraction analysis. Palladium complex **3b** was found to be active (pre)catalyst for the Suzuki cross-coupling of aryl bromides with phenylboronic acid.

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1. Introduction

Progress in coordination and organometallic chemistry is often connected with the creation of tailor-made ligand systems. In the context of the project devoted to the development of effective methodologies for oligodentate phosphorus-containing ligands for catalysis and materials science, recently we have suggested an approach based on the modular assembling of *o*-(thio)phosphorylated anilines with phosphorylacetic acid derivatives leading to P(*X*)-modified (*X* = O, S) carbamoylmethylphosphine oxides and sulfides (CMPO(*S*)) [1]. The latter acted as tridentate monoanionic pincer-type ligands upon complexation with Pd(II) and Re(I) ions owing to the ready metallation at the amide nitrogen atom, facilitated by the mutual disposition of donor centers. Obviously, the amine group in the chosen basic blocks, serving as an appropriate anchor function, can be also reacted with other carbonyl derivatives, e.g., salicylic aldehyde. As versatile ligands capable of adopting various coordination modes (both in neutral and anionic form), salicylaldimines themselves have received much attention [2]. Furthermore, the complexes of various monobasic salicylaldiminates with an ancillary chalcogen-containing donor group demonstrated high catalytic activity in the Suzuki cross-coupling [3], Heck reaction

[3a,4], oxidation of ascorbic acid [5], ethylene polymerization [6], and ring-opening polymerization of *L*-lactide [7]. While their analogs with an additional phosphine arm [8] were also shown to be effective catalysts for various processes [9], to the best of our knowledge, the literature data on the related four-coordinated phosphorus derivatives are restricted to the only one publication describing the synthesis and coordination with the Ln(III) ions (Ln = Pr, Nd) of P(O)-functionalized salicylaldimines with an elongated phosphoryl arm [10].

Herein we report on the synthesis of novel oligodentate ligands comprising mixed donor sets via modular assembling of *o*-(thio)phosphorylated anilines with salicylaldehyde and their complexing features towards transition metal ions. The preliminary catalytic studies of one of the palladium complex derived is reported.

2. Results and discussion

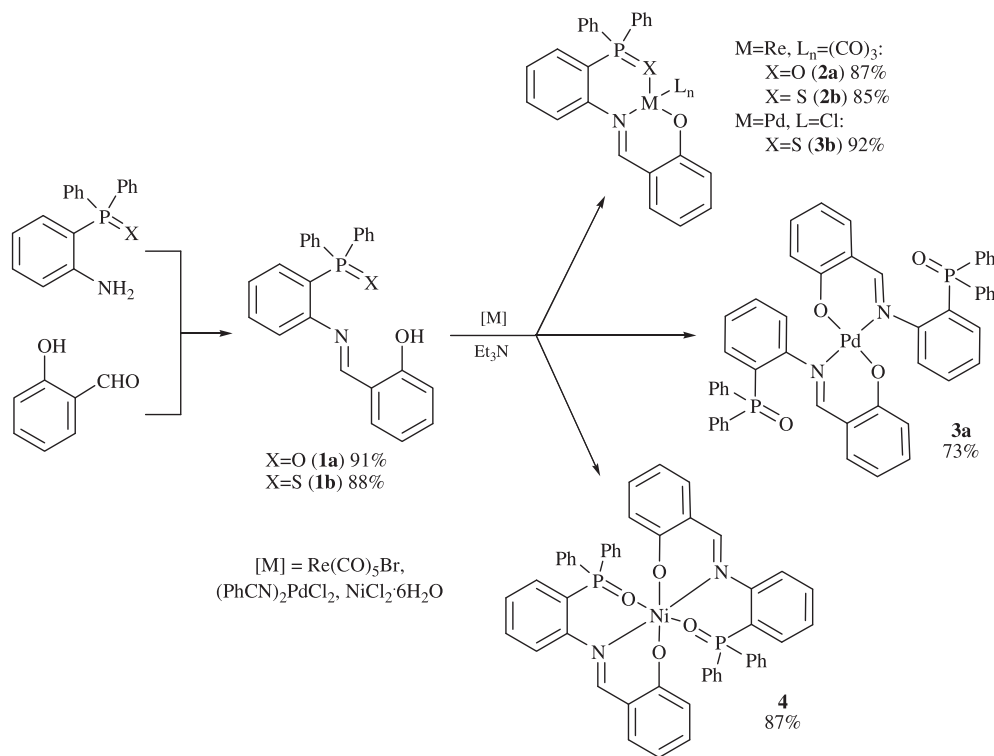
The condensation of 2-(diphenylphosphoryl)aniline and its thio analog¹ with salicylaldehyde in ethanol solution at reflux readily afforded P(*X*)-modified (*X* = O, S) salicylaldimines **1a,b** in good yields (Scheme 1). The multinuclear NMR (³¹P and ¹H) and IR spectroscopy data unequivocally confirm the formation of Schiff bases. Thus, the singlet signals of the phosphorus atoms in the ³¹P NMR spectra are observed in the regions expected for phosphine oxide (**1a**) and

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¹ For the synthesis of key (thio)phosphorylated anilines, see Ref. [1].



Scheme 1. Synthesis of salicyldimines with (thio)phosphoryl pendant arms and their complexing features.

phosphine sulfide (**1b**) derivatives (at *ca.* 27 and 41 ppm, respectively). The signals of the imine and hydroxyl protons in the ^1H NMR of **1a,b** spectra were detected at 8.46–8.56 and 11.06–11.32 ppm, respectively. The IR spectra of **1a,b** demonstrate the characteristic bands corresponding to stretching vibrations of the C=N (1613–1625 cm^{-1}) and P=X (X = O: 1194 (**1a**), X = S: 652/635 cm^{-1} (**1b**)) bonds. Note that while **1b** is stable both as solid and in solution and show no signs of decomposition for several months (as judged by the ^{31}P and ^1H NMR spectra), its oxygenated analog **1a** possesses the reduced stability even in the solid state and is gradually hydrolyzed under ambient conditions.

According to the results of X-ray diffraction analysis of **1a**, the molecule adopts a *trans*-configuration in respect to the C=N bond with the hydroxyl group oriented towards the imine fragment

(Fig. 1). Such a conformation is stabilized by the intramolecular O–H···N bond (O···N 2.6438(13) Å, OHN 148(1)°). The P=O group also points to that direction; the pseudo-torsion angle N(1)C(1)P(1)O(1) and the distance O(1)···O(2) are 57.5(1)° and 3.266(1) Å, respectively. In a crystal, the molecules are assembled into a 3D-framework through a series of weak intermolecular interactions. Those include C–H···O and C–H··· π contacts with the shortest C···O (between the phosphoryl group and CH imine fragment) and C···C separations being 3.098(1) and 3.372(1) Å, respectively.

With ligands **1a,b** in hand, it seemed interesting to estimate the effect of introduction of the P=X (X = O, S) ancillary arm on the coordination behavior of the modified salicyldimines towards transition metal ions. Thus, the reaction of **1a,b** with $\text{Re}(\text{CO})_5\text{Br}$ in toluene solution under reflux in the presence of triethylamine readily afforded complexes **2a,b** with two fused six-membered metalocycles in which the deprotonated ligand adopts a *X,N,O*-tridentate (X = O, S) coordination mode (Scheme 1). The tridentate ligation of phosphine sulfide derivative **1b** was also observed in Pd(II) complex **3b**, readily obtained by the reaction of **1b** with $(\text{PhCN})_2\text{PdCl}_2$ in dichloromethane solution at room temperature, but unlike its phosphine counterparts [8], the addition of a base (Et_3N) was found to be necessary (*vide infra*). As it could be expected, the complexation of phosphorylated salicyldimine **1a** with the same palladium precursor proceeded without participation of the P=O group oxygen atom, and in the absence of another appropriate donor center yielded $\kappa^2\text{-N,O}$ -complex **3a** with two deprotonated ligand molecules per a metal ion. At the same time, the reaction of **1a** with nickel chloride in refluxing ethanol also afforded complex of $(L\text{-H})_2\text{M}$ composition (**4**) but featuring a tridentate coordination mode of both of the ligand molecules. Interestingly, the same complex is formed as a major product also in the reaction with equimolar amounts of the reagents. Note that phosphine-substituted salicyldimines form $\kappa^3\text{-P,N,O}$ Ni(II) and Pd(II) complexes with only one ligand molecule per a metal ion [8]. In the case of complex **4**, the coordination of the second ligand

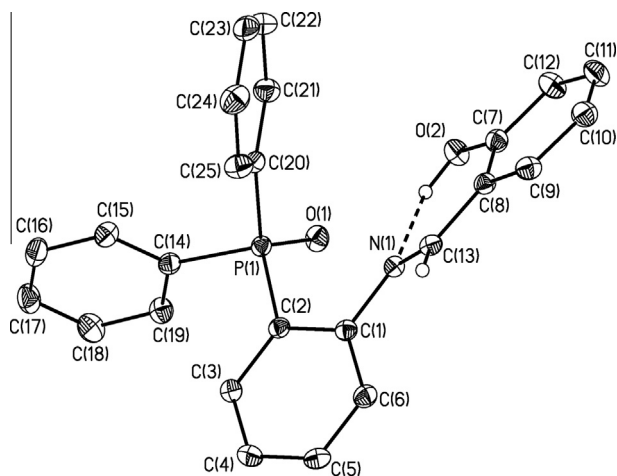


Fig. 1. General view of ligand **1a** in representation of atoms *via* thermal ellipsoids at 50% probability level. All hydrogen atoms except for those of imine and OH groups are omitted for clarity. Dashed line represents the H-bond.

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