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# Phosphorus, Sulfur, and Silicon and the Related Elements

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Effective Modular Assembling of Novel Ligands Starting from (Thio)Phosphorylated Anilines

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# EFFECTIVE MODULAR ASSEMBLING OF NOVEL LIGANDS STARTING FROM (THIO)PHOSPHORYLATED ANILINES

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**Abstract** A series of novel oligodentate ligands has been designed by the modular assembly of ortho-(thio)phosphorylated anilines with a range of commercially available carbonyl compounds. The new ligands readily form complexes with a series of metal ions (Pd(II), Cu(II), Ni(II), and Re(I)) both in neutral and deprotonated forms, providing OO, SN, ONO, SNO, SNS, SNN, and ONN donor sets. The structure and composition of the resulting complexes depend on the nature and mutual disposition of the donating groups as well as on the reaction conditions.

Keywords Oligodentate phosphorus ligands; modular assembling; transition metal complexes

## INTRODUCTION

Rational design of readily tunable ligand systems is at the heart of modern coordination chemistry. Oligodentate ligands with variable donor centers are of particular interest because they offer the opportunity of a more rigid control of the properties of a metal center

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owing to multiple options for directed structural modifications. An effective approach to complex ligand systems can be based on the modular assembling of a single basic block with a range of commercially available embedded blocks, opening the way to a whole library of ligands with diverse structures. Therewith, such a basic fragment must have an appropriate anchor function that can be used for its functionalization. Taking this into account, we decided to choose as suitable basic blocks *ortho*-phosphorylated aniline and its thio-analog. Note that the complexing features of phosphine-substituted aniline<sup>1</sup> and oligodentate ligands<sup>2</sup> on its base have been thoroughly explored, while the coordination potential of the related four-coordinated phosphorus derivatives still remains underappreciated.

#### **RESULTS AND DISCUSSION**

The key phosphorylated aniline  $1a^3$  and its thio-analog  $1b^4$  are readily available from 2-diphenylphosphinoaniline<sup>5</sup> by oxidation with H<sub>2</sub>O<sub>2</sub> and addition of elemental sulfur, respectively. Various carbonyl compounds were reacted with these basic blocks to yield novel oligodentate ligands (Scheme 1). Thus, the condensation of 1a,b with sodium enolate of benzoyl acetaldehyde led to enaminoketone derivatives 2a,b. According to <sup>1</sup>H NMR spectroscopic data, the introduction of an ancillary (thio)phosphoryl group, capable of participating in hydrogen bonding, affords the unexpected stabilization of a *trans–trans* isomer in a nonpolar solvent, such as CDCl<sub>3</sub>, and Z-s-E isomeric form in polar media (DMSO, CD<sub>3</sub>OD), which is rarely detected in the case of nonfunctionalized enaminoketones. The condensation of starting anilines with salicylaldehyde, smoothly performed in ethanol under reflux, furnished salicylaldimines 3a,b (Scheme 1). Furthermore, the reaction of thiophosphorylated aniline 1b with picolinic acid in the presence of triphenylphosphite as a dehydrating agent afforded amide 4, while the treatment of 1a,b with in situ generated dichlorosubstituted picolinic acid chloride gave its counterparts 5a,b, which can provide a







possibility of estimating additional steric and electronic factors. Finally, the direct acetylation of (thio)phosphorylated anilines **1a**,**b** with in situ generated diphenylphosphoryl acetic acid chloride or reaction of **1a**,**b** with chloroacetyl chloride followed by the treatment of the resulting chloroacetyl derivatives **7a**,**b** with Ph<sub>2</sub>PSNa resulted in novel P(X)-modified carbamoylmethylphosphine oxides (CMPO) and sulfides (CMPS) **6a–d** (Scheme 1).

The complexation features of the ligands derived were studied by the direct interaction with metal salts  $(Cu(OAc)_2 \cdot H_2O, NiCl_2 \cdot 6H_2O)$  or displacement of labile ligands from their complexes  $(Re(CO)_5Br, (PhCN)_2PdCl_2)$ , preformed either in the presence of a base (mostly in the case of Re(I) derivatives) or without a base. Thus, the reaction of P(X)modified (X = O, S) ketoenamines **2a,b** with Re(I), Pd(II), Ni(II), and Cu(II) precursors readily afforded complexes with two six-membered fused metallocycles, in which the ligands adopt a tridentate monoanionic coordination mode (Scheme 2). Therewith, the composition of the resulting complexes depended on the substituent X at the P(X)-group in **2a,b**. Note that in all cases the deprotonated ligands were stabilized in the Z-s-Z isomeric form.

Salicylaldimines **3a**,**b**, in which the donor group amenable to deprotonation is shifted to the side, also readily formed complexes of different compositions in the presence of Et<sub>3</sub>N (except for Cu(II) complex), in each case featuring  $\kappa^3$ -XNO monoanionic coordination mode (Scheme 3).

Note that both the palladium and copper complexes can be obtained by the template assembling of starting anilines **1a**,**b** and salicylaldehyde on the metal ion. At the same time, the reaction of **1a** with salicylaldehyde copper complex was found to be slow enough to enable isolation of a half-condensation product. Owing to the presence of the salicylaldehyde entity, the latter can be reacted with other primary amines, leading to unsymmetrical Schiff-base products (Scheme 4).





Both unsubstituted thiophosphorylated picolinylamide **4** and its dichlorinated analogs **5a,b** readily underwent metallation at the nitrogen atom in reactions with Re(I) and Cu(II) precursors to form 5,6-membred  $\kappa^3$ -*SNN* complexes (Scheme 5). Again the nature of the substituent X at the phosphorus atom affected the composition of the final products. The effect of additional steric hindrances in the case of ligand **5b** was best manifested for the palladium derivative, leading only to the bidentately bonded complex, lacking the coordination of the pyridine moiety, while its unsubstituted counterpart **4** readily afforded  $\kappa^3$ -*SNN* complex.

The reaction of carbamoylmethylphosphine oxides and sulfides **6a–d** with the Re(I) and Pd(II) precursors easily furnished  $\kappa^3$ -*XNY* complexes with two six-membered fused metallocycles (Scheme 6). Thus, unlike the known CMP derivatives, the coordination of a carbamoyl moiety occurs via the nitrogen atom rather than the oxygen atom. The interaction of **6a** with Re(CO)<sub>5</sub>Br without addition of a base gave  $\kappa^2$ -*OO* ten-membered metallocycle lacking the coordination of an amide fragment. This molecular complex can be readily transformed into  $\kappa^3$ -*ONO* complex with the deprotonated ligand under the action of Et<sub>3</sub>N, and, therefore, is likely to be considered as an intermediate in the reaction with the base.



#### CONCLUSION

To summarize the results presented, simple modular assembling procedures of the available building-blocks, *ortho*-(thio)phosphorylated anilines, and a number of carbonyl derivatives afforded several series of oligodentate ligands with donor centers of variable nature, therewith, offering ample opportunities for fine-tuning of their electronic and steric properties. The ligands derived show wide coordination diversity, forming complexes with different metal ions both in neutral and deprotonated forms, depending on the nature of donating groups, metal ions, and reaction conditions.

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