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Coordination of P(X)-modified (X = O, S) *N*-aryl-carbamoylmethylphosphine oxides and sulfides with Pd(II) and Re(I) ions: Facile formation of 6,6-membered pincer complexes featuring atropisomerism

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ABSTRACT

Direct acetylation of (thio)phosphorylated anilines **1a**,**b** with *in situ* generated $Ph_2P(O)CH_2C(O)Cl$ or sequential treatment of **1a**,**b** with chloroacetyl chloride and Ph_2PSNa resulted in novel oligodentate ligands, namely, P(X)-modified carbamoylmethylphosphine oxides (CMPO) and sulfides (CMPS) **2a**–**d**. In reactions with $Re(CO)_5Br$ (in the presence of Et_3N) and $(PhCN)_2PdCl_2$ these ligands afforded κ^3-*XNY* (*X*,*Y* = *O*,*S*) Re(I) (**4a**,**d**) and Pd(II) (**6b**–**d**) pincer complexes with two fused six-membered metallocycles, owing to ready metallation at the amide nitrogen atom. In the absence of a base, the interaction of **2a** with the same rhenium precursor yielded ten-membered κ^3-*OO* metallocycle **5** with Re(I) ion coordinated only by phosphoryl groups. According to the NMR spectroscopy data, the complexes obtained form stable atropisomers in solution at room temperature. The solid state structures of compounds **2a**,**b** and resulting metallocycles were characterized by X-ray crystallography.

1. Introduction

Organophosphorus compounds amount to the most important ligands in inorganic and organometallic chemistry, playing an indispensable role both in homogeneous catalysis and different metal separation processes. In particular, various phosphoryl-containing substances found wide application in the recovery of rare-earth elements from acidic radioactive liquid wastes [1]. The main advances in this field over more than semicentury history pertain to the development of bidentate ligands, namely, carbamoylmethylphosphine oxides (CMPO) of general formula $R^1{}_2P(O)CH_2C(O)NR^2R^3$ [2] which were proved to be the most preferable extractants in terms of availability, cost, and extraction efficiency. While a priority was continuously placed on CMPO and related phosphoryl-containing derivatives, their thiophosphoryl analogs have received far less attention [3].

Carbamoylmethylphoshoryl derivatives usually serve as neutral bidentate ligands bounding to a metal center through the oxygen atoms of amide and phosphoryl groups [4]. It is natural to assume that the introduction of ancillary donating arm(s) may strongly affect the coordination behavior of modified CMPO compounds. Thus, the condensation of *ortho*-phosphorylated aniline and its thioanalog with phosphorylacetic acid derivatives would lead to oligodentate ligands in which the P=X (X = O, S) group of aniline fragment could serve as a useful directing group for metallation at the amide nitrogen atom of carbamoylmethyl(thio)phosphoryl moiety, thereby, resulting in a pincer-type tridentate monoanionic framework. Pincer complexes comprise a unique class of organometallic compounds that receives growing attention in catalysis, materials science and many other fields [5,6]. Unfailing interest to these derivatives stems from the presence of multiple sites for directed structural modifications offering ample opportunities for fine-tuning of their steric and electronic properties. While most of organophosphorus pincer-type ligands relate to trivalent phosphorus derivatives (phosphines, phosphinites, phosphites and so on), recently we have shown that thiophosphoryl-containing ligands bearing the four-coordinated phosphorus center can successfully compete in catalytic performance with their P(III) counterparts [7].

Herein we report on the facile synthesis of novel tridentate ligands by the modular assembling of *ortho*-(thio)phosphorylated anilines with CMPO(S) precursors which provide upon complexation with Re(I) and Pd(II) precursors *ONO*, *SNO*, and *SNS* donor sets due to the N–H bond activation of a CMPO(S) fragment, resulting in 6,6-membered pincer complexes.

2. Results and discussion

2.1. Synthesis of ligands

The key phosphorylated aniline **1a** [8] and its thioanalog **1b** [9] are readily accessible from 2-diphenylphosphinoaniline [10] by

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oxidation with H_2O_2 and addition of elemental sulfur, respectively. To anchor a CMPO(S) fragment on the aniline scaffold, two different synthetic approaches have been developed, depending on the nature of the substituent X in the P=X group of a carbamoylmethyl moiety (Scheme 1). The first route (compounds **2a**,**b**) consisted in the acylation of the starting anilines **1a**,**b** with diphenylphosphorylacetic acid chloride generated *in situ* from the corresponding acid using PCl_3 as a mild chlorinating agent via the general procedure previously developed in our laboratory [11]. The second approach used for the synthesis of CMPS derivatives **2c**,**d** was based on the reaction of starting anilines **1a**,**b** with chloroacetyl chloride followed by the treatment of the resulting chloroacetyl derivatives **3a**,**b** with sodium diphenylthiophosphinite. The methods employed (Scheme 1) afforded the desired ligands **2a**–**d** in moderate to good yields (55–79%).

The structures of ligands **2a**–**d** as well as intermediate derivatives **3a**,**b** were unambiguously confirmed based on the multinuclear NMR (^{31}P, ^{1}H, and ^{13}C) and IR spectral data. The ^{31}P NMR spectra of **2a**–**d** show two singlet signals in the regions typical for these classes of organophosphorus compounds. Thus, the signals of the phosphorus resonances of phosphoryl group in $ArP(O)Ph_2$ (**2a**,**c**) and carbamoylmethyl (**2a**,**b**) fragments were observed at ~37 and 27–28 ppm, respectively, while in the case of thiophosphoryl derivatives (**2b**–**d**) the signals of P=S groups were manifested in a narrow range from 38 to 40 ppm independent from the nature of an additional substituent in the $-P(S)Ph_2$ moiety. The presence of a great number of phenyl rings in the molecules of these acetamides complicates the interpretation of ^{1}H NMR spectra in the region typical for aromatic proton signals, however, the signals of the hydrogen atoms of an amide group and doublet signals of the protons of a methylene unit can be easily identified: δ_{NH} 9.92–11.29, δ_{CH2} 3.04–3.61 ppm ($^{2}J_{HP} \sim 14–15$ Hz). The ^{13}C NMR spectral data of compounds **2a**–**d** are also well consistent with the proposed structures: e.g., δ_{CH2} 41–45 ppm ($^{1}J_{PC} = 47–63$ Hz), $\delta_{C(O)NH2} \sim 163$ ppm ($^{2}J_{PC} \sim 5$ Hz). Moreover, unlike the proton spectra, the signals of the carbon atoms of a central benzene ring, as a rule, do not overlap with those of C_{Ph}-atoms of peripheral phenyl moieties (see Section 4). The IR spectra of crystalline samples of **2a**–**d** demonstrate the characteristic stretching vibrations of the carbonyl group (ν(C=O) 1677–1690 cm^{-1}) and N–H bond (ν(NH) 3200–3300 cm^{-1}), whereas the absorption bands typical for the secondary amides and associated mainly with the deformational vibrations of N–H bond are observed in the range from 1500 to 1540 cm^{-1}. The position of absorption bands corresponding to the phosphoryl and thiophosphoryl group vibrations depends on the nature of an additional substituent at the phosphorus atom (aryl or alkyl). Thus, the absorption bands of phosphoryl group of a CMPO moiety are observed at 1198/1203 (**2a**) and 1202 (**2b**) cm^{-1}, while ν(P=O) of triarylphosphine oxide moiety – at 1160/1167 (**2a**) and 1153/1167 (**2c**) cm^{-1}. Analogously, in the case of thiophosphoryl derivatives: ν(P=S) for $ArP(S)Ph_2$ appears in the lower frequency region than that for $CH_2P(S)Ph_2$ fragment (*cf.* 614/637 and 649 cm^{-1}, respectively, in the case of *SNS* ligand **2d**). Note that the observation of several bands corresponding to stretching of the P=O bond as well as broadening of the amide group characteristic vibrations are likely to be connected with the formation of intra- and intermolecular hydrogen bonds.

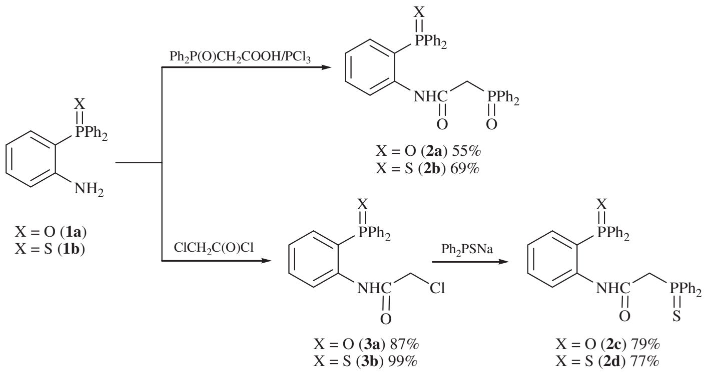
According to the X-ray diffraction data, ligands **2a** (the crystallosolvate with water and ethanol, 0.5 each per one molecule of the product) and **2b** possess quite typical geometrical parameters for the molecules of this type (Fig. 1). Note that the pseudo-torsion angle O(1)P(1)C(2)C(1) in the molecule of **2a** comprises 34.0(1)°. Such a position of the P=O bond respective to the benzene core in the $ArP(O)Ph_2$ fragment is apparently governed by the intramolecular H–bond with the NH group (Fig. 1; N(1)–H(1N) 0.92 Å, H(1N)···O(1) 1.98 Å, N(1)···O(1) 2.782(2) Å, NHO 145(1)°). In **2b**, the same value for the P(1)=S(1) group, which is not such a convenient proton-acceptor as P=O one, is 64.3(1)°.

The CMP-coordination arm in the molecules of **2a** and **2b** is geometrically very similar to that in non-functionalized *N*-arylcarbamoylmethylphosphine oxides, $Ph_2P(O)CH_2C(O)NHAr$ [11], the most pronounced difference being the values of the angle O(2)P(2)C(1)C(2) equal to 57.3(1) and 63.6(1)° in **2a** and **2b**, respectively, and 16–30° in the molecule of $Ph_2P(O)CH_2C(O)NHAr$ or its bis-CMP analog 1,3-$[Ph_2P(O)CH_2C(O)NH]_2C_6H_4$ [11], also due to the differences in the H-bonding patterns. Thus, the P=O group of a CMPO fragment in **2b** is involved in the intramolecular H-bond with the only NH group in a molecule (Fig. 2; N(1)–H(1N) 0.91 Å, H(1N)···O(2) 2.06 Å, N(1)···O(2) 2.7996(17) Å, NHO 138(1)°). In the crystal of **2a**, out of the two symmetry-identical molecules of the ligand in a unit cell, the P=O group of a CMPO moiety forms the H-bond with the hydrate water molecule through the P(2)=O(2) bond (O(1W)···O(2) 2.65(1) Å, OHO ~ 165°), while the other P=O group form hydrogen bond with ethanol molecule (O(1S′)···O(1) 2.80(1) Å, OHO ~ 145°) and the intramolecular H-bond with the amide hydrogen (N(1)–H(1N) 0.92 Å, H(1N)···O(1) 1.98, N(1)···O(1) 2.782(2) Å, NHO 145(1)°). Therefore, the pattern of H-bonds in **2a** and **2b** ensure the cisoid disposition of the P=X groups, which was expected for their complexes only (*vide infra*).

Various weak interactions such as C–H···X (X = O in **2a** and X = O, S in **2b**), C–H···π and H···H as well as O···π in **2b** hold the molecules in these crystals.

2.2. Synthesis of complexes

While studying the complexation features of the ligands derived, it was found that the reaction of **2a**,**d** with rhenium pentacarbonyl bromide in toluene solution under reflux in the presence of triethylamine indeed readily proceeds as the metallation at the nitrogen atom of an amide fragment accompanied by



Scheme 1. Synthesis of (thio)phosphoryl-substituted carbamoylmethylphosphine oxides **2a**,**b** and sulfides **2c**,**d**.