



Synthesis and characterization of novel phosphinamide bidentate ligands with groups P=O, P=S and P=Se: Application in coordination chemistry with Zn⁺⁺

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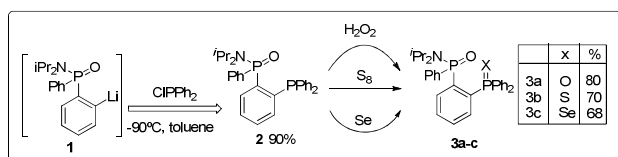
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INTRODUCTION

Hemilabile ligands possessing two or more donor atoms with very different electronic properties close to the metal represent a very active research field. The binding of the metal to a chelating ligand containing hard and soft donor atoms allows for the easy displacement of the labile group providing access to an open coordination site in a reversible manner. These features make hemilabile ligands very interesting in a number of fields including coordination chemistry and metal complex catalysis.¹ The current work presents a comprehensive study on the synthesis of novel phosphinamide bidentate ligands **3a-c** employing directed *ortho*-lithiation methodology^{2,3} (Scheme 1) and subsequent complexation with zinc chloride.

RESULTS AND DISCUSSION

Intermediate **2** was obtained in 90% yield by *ortho* lithiation of the diphenylphosphinamide **1** at low temperature followed by coupling with chloro diphenylphosphine as the electrophile. Oxidation of the phosphino group *in situ* with H₂O₂, S and Se gave rise to the hemilabile bidentate ligands **3a-c** in yields ranging from 60-90% (Scheme 1).



Scheme 1. Synthesis of ligands (**3a-c**) through transformations of *ortho*-functionalized phosphinic amides.

Table 1 shows the characterization of the three compounds by ³¹P-NMR and HRMS. Single crystals of **3b** and its complex with ZnCl₂ were obtained through slow vapors diffusion of diethyl ether into a solution containing the compound in CH₂Cl₂/ACN (1:1) and are represented in Figure 1.

Table 1. Characterization of ligands **3a-c** by ³¹P-NMR and HRMS (ESI).

Ligands	³¹ P-NMR δ (ppm)	HRMS (ESI)
3a	28.70 (d, ³ J _{PP} 4.4 Hz, P=O), 50.71 (d, ³ J _{PP} 4.7 Hz, P=S).	502.2020 (MH ⁺), found: 502.2066.
3b	28.70 (d, ³ J _{PP} 4.4 Hz, P=O), 50.71 (d, ³ J _{PP} 4.7 Hz, P=S).	518.1792 (MH ⁺), found: 518.1813.
3c	28.46 (d, ³ J _{PP} 4.0 Hz, P=O), 42.38 (d, ³ J _{PP} 4.0 Hz, P=Se).	566.1281 (MH ⁺), found: 566.1288.

Crystal data:

Ligand 3b (C₃₀H₃₃NP₂OS, CH₃CN): Triclinic; P-1; a=9.1412(13); b=9.8502(17); c= 17.910(4) Å; α=93.263(18)°; β=94.429(17)°; γ=109.92(2)°; n° reflections/parameters = 5481/334; R₁=4,8%; S = 0,92. Temperature 298K.

Complex 3b-Zn (C₃₀H₃₃NP₂OSZnCl₂): Monoclinic; P2₁/c; a=10.7119(3); b=15.7322(7); c=18.1799(7) Å; β=93.429(3)°; n° reflections/parameters = 5572/343; R₁=3,1%; S = 1,15. Temperature 100K.

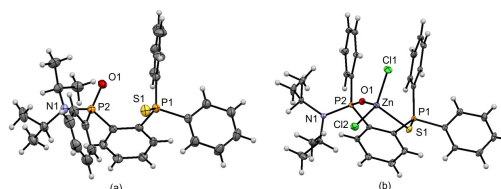


Figure 1: Representation of crystalline structure of ligand **3b** (a) and its Zn complex (b).

CONCLUSION

The bidentate ligands **3a-c** were obtained in good yields and unequivocal characterization. X-ray analysis for **3b** and **3b-Zn** showed distortion of the phenyl group, as well as the change from monoclinic crystal system to triclinic, respectively.

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