



Synthesis of new hemilabile ligands based on phosphinic amide and pyrazolo[1,5-c]quinazoline moieties Applications in coordination chemistry

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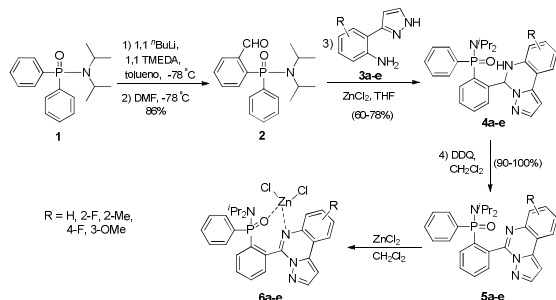
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INTRODUCTION

We have previously shown that bis(phosphinic amide)-phosphine oxides can be accessed via directed ortho lithiation (DoM) of phosphinic amides.¹ The tridentate ligand was the basis for the development of membrane and optical fiber luminescence sensors.² We envisaged that this methodology could be extended to the synthesis of new hemilabile O,N-chelating ligands. Here we describe the preparation of pyrazoloquinazoline-phosphinic amide ligands through condensation of o-formylphosphinic amides with 2-pyrazolylanilines followed by oxidation and their complexation behavior towards zinc salts.

RESULTS AND DISCUSSION

Pyrazolo[1,5-c]quinazoline-phosphinic amides (5a-e) were synthesized in a three step process consisting of o-formylation of diphenylphosphinic amide (1), condensation with 2-pyrazolylanilines (2) catalyzed by ZnCl₂ and oxidation of the resulting dihydro-pyrazoloquinolines (4a-e) using 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), to the desired products (5) (Scheme 1).



Scheme 1. Synthetic route to Pyrazolo[1,5-c]quinazoline-phosphinic (5a-e) and their Zn(II) complexes (6a-e).

All new compounds were characterized by HR-MS, IR, ¹H, ¹³C and ³¹P NMR spectroscopy. The metal-binding abilities of compounds (5) towards Zn(II) cations were investigated. Preliminary results indicate that coordination to the metal cation takes place through the oxygen of the phosphinic amide and the nitrogen of the quinazoline moiety.

CONCLUSION

An efficient methodology for the synthesis of pyrazolo[1,5-c]quinazoline-phosphinic amides (5a-e) has been developed. They behave as O,N-chelating ligands towards zinc dichloride through formation of seven-membered N-Zn-O metallacycles (6a-e). Further applications of the ligands in catalysis are currently under investigation in our laboratory.

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