NMR Studies of Di- and Mononuclear Copper (I) Complexes Containing the (*S, S*)-^{i}Pr-Pybox Ligand

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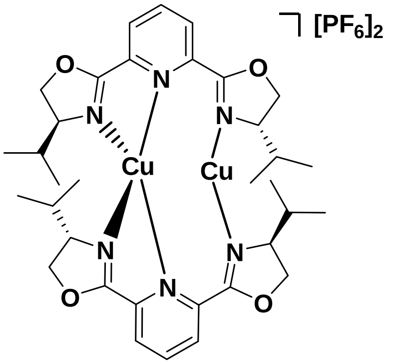
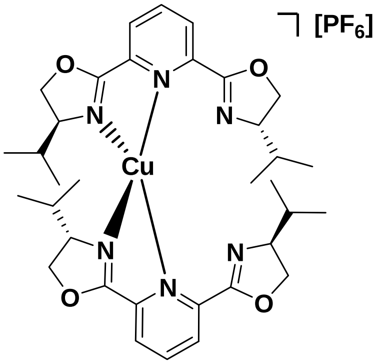
The reaction of $[Cu(CN)_4]PF_6$ with (*S,S*)-^{i}Pr-Pybox affords the dinuclear Cu (I) cationic complex (**1**) or the Cu(I) cationic complex (**2**) when appropriate stoichiometric amounts of the pybox ligand are used. These compounds have been characterized by mass spectrometry and the nuclearity of the complex **1** has been established through X-ray crystallographic studies.[1] The preliminary NMR study of these compounds showed that their structures are not maintained in the solution state, since ^{1}H and ^{13}C NMR spectra of both di- and mononuclear complexes are consistent with the presence of a C_2 symmetry axis.



1



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The dinuclear complex **1** has been successfully used as a precatalyst for the enantioselective synthesis of propargylic amines (unpublished results). In order to understand its catalytic behaviour it seemed necessary to gain some knowledge of the species that this compound produces in solution. To this aim, an NMR study of both di- and mononuclear copper (I)-$(pybox)_2$ complexes in the solution state was accomplished. Titration of the dinuclear Cu (I) complex with an excess of (*S,S*)-^{i}Pr-Pybox, together with variable temperature ^{1}H NMR experiments, ^{1}H, ^{19}F and ^{31}P dosy experiments, and ^{1}H^{19}F HOESY measurements conclude that compounds **1** and **2** exist as stable, discreet molecules in solution with the copper nuclei being rapidly exchanged among the ^{i}Pr-pybox nitrogen atoms.

On the other hand, some di- and mononuclear copper (I)-(^{i}Pr-pybox) complexes carrying phosphines (Ph_3P, dppm, diphenylphosphinoferrocenyl) as a second ligand have also been synthesized for the first time and their characterization in the solution state by NMR has been carried out as an initial survey of their potential catalytic properties.

[1] Díez, J., Gamasa, M. P., Panera, M., *Inorg. Chem.* 2006, *45*, 10043-10045.