Functionalized thiosemicarbazone ligands and their complexes

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Abstract - The purpose of this work is the design, synthesis and characterization of thiosemicarbazone ligands bearing a phenyl boronic acid functionality. The main interest is the synthesis of organopalladium compounds with the boronic acid included within the corresponding molecule. These could lead to further modification of the properties of the organometallic species applicable to the Suzuki-Miyaura reaction.

The ligands were prepared by reaction of acetylphenylboronic acid with several thiosemicarbazides. The compounds were characterized by IR, ^{1}H and ^{31}P NMR spectroscopy.

Keywords - Boronic Acid, Catalysis, Suzuki, Thiosemicarbazone, Ligand, Metal, Characterization

Introduction

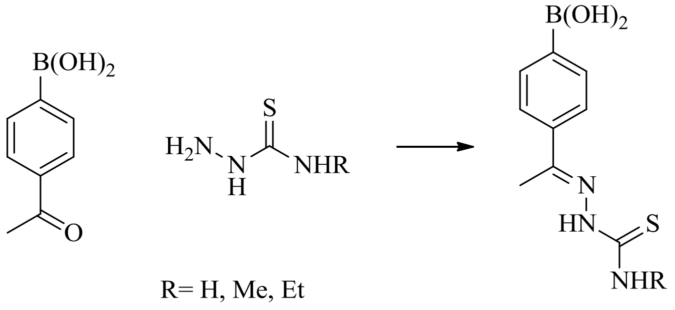
Thiosemicarbazones are versatile ligands which are able to coordinate to metals through C, N and S atoms. When bonding to the metal is through the sulfur, iminic nitrogen and a carbon atoms cyclometallated compounds are formed. These have aroused great interest due to their wide range of applications. Their biological activity depends on the parent aldehyde or ketone [1-2]; also, palladium (II) complexes have shown to be catalytically active in the Heck and Suzuki-Miyaura cross-coupling reactions[3-4].

Previous studies have shown the tetranuclear structure of these compounds [5-6], which implies a low solubility in the common organic solvents, limiting their potential applications. For this reason we pursue tetranuclear compounds with better solution properties by using different organic precursors; in this particular case an organic precursor bearing the boronic acid functionality.The boronic acid could lead to further modification of the structure of the cyclometallated tetranuclear compound using the Suzuki cross-coupling reaction.

Herein we report the synthesis of a series of cyclometallated compounds derived from a boronic thiosemicarbazone.

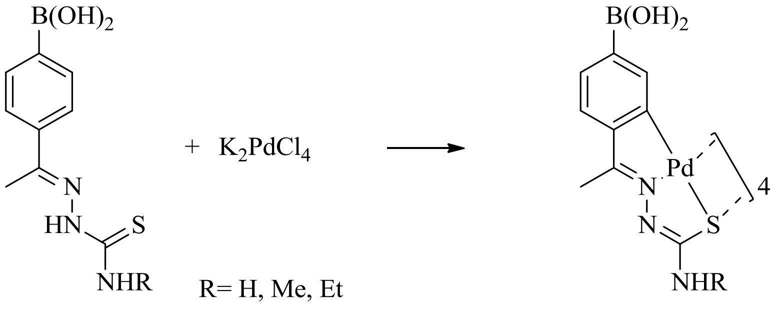
Results and discussion

The synthesis of the ligands is shown in Scheme 1.



Scheme 1

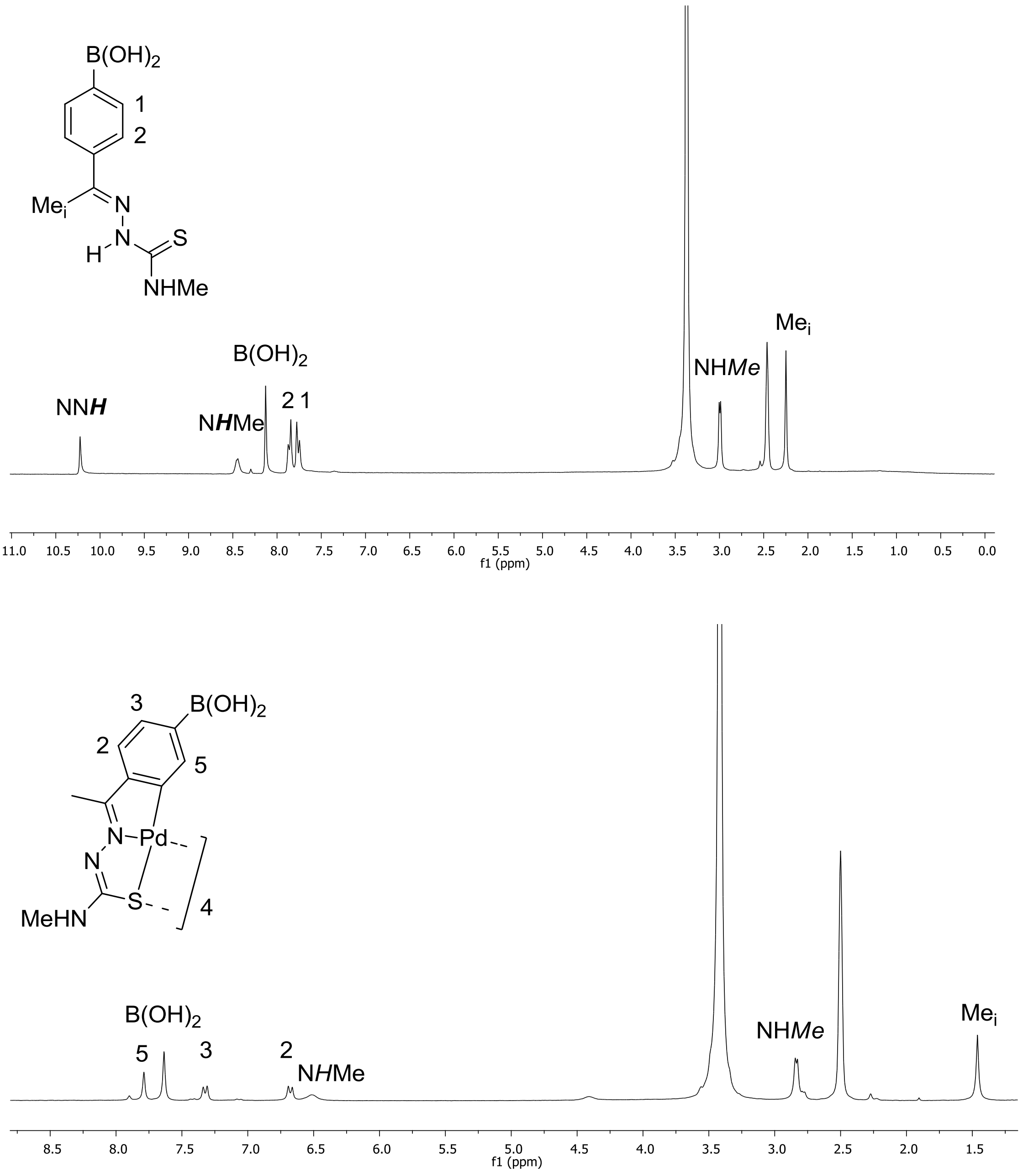
The reaction of the ligands with potassium tetrachloropalladate gave the corresponding Pd(II) compounds; in which the ligands are bonded to the metal through the *ortho*-C of the phenyl ring and coordinated to the metal by the nitrogen and sulfur atoms. Each palladium atom is bonded to two different sulfur atoms, forming two types of bonds: Metal-$S_{chelate}$ and Metal-$S_{bridging}$. (Scheme 2)



Scheme 2

The ^{1}H NMR spectra of the ligands and their corresponding Pd(II) compounds confirmed the formation of the species and gave information on their structure.

In the spectra of the ligands a singlet signal *ca*. 10.2 ppm was assigned to the hydrazinic proton and AA'BB' system ca. 7.75 ppm to the phenyl protons (4H). In the spectra of the compounds, hydrazinic proton resonance is absent in accordance with coordination in the thiolic form. Metallation is evidenced by changes in the aromatic region.



^{1}H NMR spectrum of ligand L2 and the corresponding compound C2.

The IR spectra of the ligands showed bands for the C=S group and hydrazinic N-H stretch, which are absent in the spectra of the compounds, confirming the deprotonation of the thiosemicarbazone and the coordination in the thiolic form.

The shift of the ν(C=N) band implies coordination is through the nitrogen lone pair and not through the C=N double bond.

IR data.

COMPOUND	ν(C=N)	Δ(C=N)	ν(C=S)	ν(N-H)	ν(B-O)	ν(O-H)
L1	1595	-	831	3314, 3341	1363	3500
C1	1578	17	-	3256	1382	3446
L2	1592	-	819	3317, 3321	1357	3450
C2	1577	15	-	3341	1345	3427
L3	1596	-	813	3272, 3330	1352	3458
C3	1570	26	-	3354	1350	3437

Experimental

The ligands were prepared by the condensation of acetylphenylboronic acid with different thiosemicarbazides. Acetylphenylboronic acid and hydrochloric acid (35 %) were added to a suspension of the corresponding thiosemicarbazide in water (25 cm^3) to give a clear solution, which was stirred at room temperature for 4 h. The white solid that precipitated was filtered off, washed with cold water and dried in air.

The palladium compounds were prepared by the addition of a solution of K_2PdCl_4 in water to a ethanolic solution of the ligand, as appropiate. The reaction mixture was then kept at room temperature for 24 h. The precipitated yellow solids were filtered, redisolved in DCM and filtered. The solvent was eliminated to yield the compounds in 78-88% yield.

Acknowledgements

We wish to thank the financial support received from the Xunta de Galicia (Galicia, Spain) under the Grupos de Referencia Competitiva Programme Projects GRC2015/009.

F. Reigosa and F. Lucio thank the Spanish Ministry of Education (grant FPU15/07145 and FPU13/05014)

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