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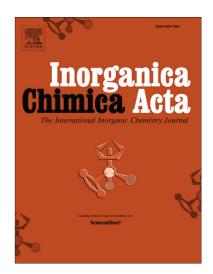
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ACCEPTED MANUSCRIPT

Alkoxylation of the imine carbon atom of a Schiff-base ligand upon coordination to arene ruthenium

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Abstract

The Schiff-base 5-methyl-4-{(pyridin-2-ylmethylene)amino}-4H-1,2,4-triazole-3-thiol (L-H) reacts in alcoholic solution (methanol, ethanol, isopropanol) at room temperature with the dinuclear precursor $[(\eta^6\text{-MeC}_6H_4\text{Pr}^i)\text{RuCl}_2]_2$ to give a series of neutral complexes of the general formula $(\eta^6\text{-MeC}_6H_4\text{Pr}^i)\text{Ru}(\text{L-OR})$ (R = Me, 1; R = Et, 2; R = Prⁱ, 3). In these complexes, the Schiff-base ligand coordinates to the arene ruthenium unit in a *S,N,N*-tridentate fashion and concomitantly to the coordination process a nucleophilic addition of the alcohol occurs on the imine carbon of L, thus forming the corresponding L-OR ligand. The molecular structure of 3, solved by single-crystal X-ray analysis, shows a piano-stool arrangement with the *p*-cymene, the S_{thiolato}, the N_{imine} and N_{pyridyl} surrounding the chiral-atmetal ruthenium center and an OPrⁱ group attached to the imine carbon. The insertion of an alkoxy group on the carbon atom reduces the imine function and introduces chirality on the ligand, thus generating a second chiral center and potentially diastereoisomeric complexes. However, steric hindrance on the ligand forces the formation of only one pair of enantiomers.

Keywords: Arene ruthenium complexes; Nucleophilic addition; Schiff-base ligand; Half-sandwich complexes.

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