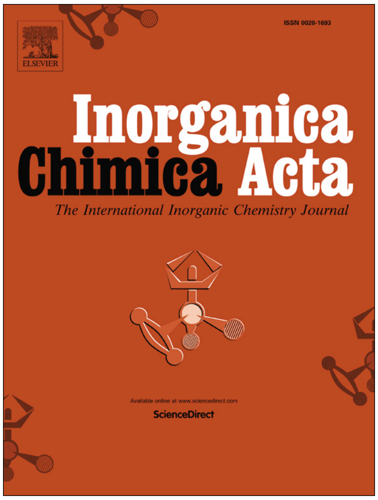

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Alkoxylation of the imine carbon atom of a Schiff-base ligand upon coordination to arene ruthenium

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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 $[(\eta^6\text{-MeC}_6\text{H}_4\text{Pr}^i)\text{RuCl}_2]_2$ to give a series of neutral complexes of the general formula $(\eta^6\text{-MeC}_6\text{H}_4\text{Pr}^i)\text{Ru(L-OR)}$ (R = Me, **1**; R = Et, **2**; R = Pr^i, **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 $\text{S}_{\text{thiolato}}$, the N_{imine} and $\text{N}_{\text{pyridyl}}$ surrounding the chiral-at-metal ruthenium center and an OPr^i 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.