Abstract

A series of new arene ruthenium(II) complexes were prepared by reaction of ruthenium(II) precursors of the general formula $[(\eta^6-\operatorname{arene})\operatorname{Ru}(\mu-\operatorname{Cl})\operatorname{Cl}]_2$ with N,N'-bidentate pyridyl-imine ligands to form complexes of the type $[(\eta^6-\operatorname{arene})\operatorname{Ru}\operatorname{Cl}(\operatorname{C}_5\operatorname{H}_4\operatorname{N}_2-\operatorname{CH}=\operatorname{N}-\operatorname{R})]\operatorname{PF}_6$, with arene = $\operatorname{C}_6\operatorname{H}_6$, R = iso-propyl (**1a**), *tert*-butyl (**1b**), cyclohexyl (**1c**), cyclopentyl (**1d**) and *n*-butyl (**1e**); arene = *p*-cymene, R = iso-propyl (**2a**), *tert*-butyl (**2b**). The complexes were fully characterized by ¹H NMR and ¹³C NMR, UV–Vis and IR spectroscopies, elemental analyses, and the single-crystal X-ray structures of **2a** and **2b** have been determined. The single-crystal molecular structure revealed both compounds with a pseudo-octahedral geometry around the Ru(II) center, normally referred to as a piano stool conformation, with the pyridyl-imine as a bidentate N,N ligand. The activity of all complexes in the transfer hydrogenation of cyclohexanone in the presence of NaOH and iso-propanol is reported, the compounds showing turnover numbers of close to 1990 and high conversions. Complex **2b** was also shown to be very effective for a range of aliphatic and cyclic ketones, giving conversions of up to 100 %.