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Borate-based ligands with soft heterocycles and their ruthenium complexes

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Abstract:

In a quest for effective synthetic precursors for the preparation of B-agostic complexes of ruthenium, we have shown that the reaction of $[\text{Cp}^*\text{RuCl}_2]_2$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) with $[\text{NaBt}]$ or $[\text{NaBo}]$ ($\text{Bt} = \text{dihydrobis(2-mercaptobenzthiazolyl)borate}$; $\text{Bo} = \text{dihydrobis(2-mercaptobenzoxazolyl)borate}$) led to the formation of B-agostic complexes $[\text{Cp}^*\text{RuBH}_2\text{L}_2]$, **1a,b** (**1a**: $\text{L} = 2\text{-mercaptobenzthiazol}$, **1b**: $\text{L} = 2\text{-mercaptobenzoxazol}$) and $[\text{Cp}^*\text{RuBH}_3\text{L}]$, **2a,b** (**2a**: $\text{L} = 2\text{-mercaptobenzthiazol}$, **2b**: $\text{L} = 2\text{-mercaptobenzoxazol}$) in good yields. In parallel to the formation of **1a,b** and **2a,b**, this method also allowed the formation of ruthenium hydrotrisborate complexes $[\text{Cp}^*\text{RuBYL}_3]$, **3a-c** (**3a**: $\text{L} = 2\text{-mercaptobenzthiazol}$, $\text{Y} = \text{H}$; **3b**: $\text{L} = 2\text{-mercaptobenzoxazol}$, $\text{Y} = \text{H}$; **3c**: $\text{L} = 2\text{-mercaptobenzoxazol}$, $\text{Y} = \text{Cl}$). The key feature of complexes **3a-c** is the coordination of one of the 2-mercaptobenzothiazole ligand that connects to the metal and the boron centre through a common sulfur atom. Upon heating, compounds **3a,b** change into their corresponding S→N linkage isomers, in which the boron atom is bonded to three nitrogen atoms. The cyclic voltametric studies on compounds **3a-c** and **4a,b** suggest that a deviation in coordination of the

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