

Steric control of the coordination mode of thiosemicarbazone ligands, synthesis, structure and redox properties of ruthenium and osmium complexes

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An unusual coordination mode (**1**) of benzaldehydethiosemicarbazone (Hbztsc-R) has been observed in a series of complexes of type $[M(PPh_3)_2(bztsc-R)_2]$ ($M = Ru, Os$) obtained from the reaction of the ligands with $[M(PPh_3)_2X_2]$ ($X = Cl, Br$). Assuming the bulk of PPh_3 to be responsible for such a coordination mode, another family of mixed-ligand complexes of type $[M(bpy)_2(bztsc-R)]^+$ have been prepared where 2,2'-bipyridine, which is of much smaller size, has been used as the co-ligand. However, similar four-membered chelate ring formation by benzaldehydethiosemicarbazone (**1**) has been observed. Modelling studies have showed that this mode of coordination of the benzaldehydethiosemicarbazone ligand depends on the steric bulk of the aryl group. This has been authenticated by preparing similar complexes of acetone-thiosemicarbazone (Hactsc), viz. $[M(bpy)_2(actsc)]^+$, where the actsc ligand forms a five-membered chelate ring (**2**). Structures of a selected benzaldehydethiosemicarbazone ligand and three representative complexes have been determined. Spectral and electrochemical properties of the complexes have been investigated.

