Mono- and Bis-Methyltrioxorhenium(VII) Complexes with Salen Ligands: Synthesis, Properties, Applications

Abstract:
Methyltrioxorhenium(VII) (MTO) forms 1:1 (mono-) or/and 2:1 (bis-) complexes with salen ligands, undergoing a hydrogen transfer from a ligand-bound OH-group to a ligand nitrogen atom. Some complexes show good stability both in the solid state and in solution, while others must be kept at low temperatures under an argon atmosphere. X-ray crystallography shows distorted trigonal bipyramidal structures of all examined complexes in the solid state, this structure being due to the steric demands of the ligands, with the methyl group of MTO residing in the apical sites in the cis position. Temperature-dependent proton NMR data indicate that the coordination between salen ligands and MTO at low temperatures is considerably stronger than at room temperature. Density functional theory calculations have been performed to find approximate structures for all described complexes and to try to find a rationale for the preferred formation of mono-versus bis-MTO complexes. The formation of mono- or bis-MTO adducts is dependent on both the steric and the electronic influence of the respective salen ligands. The catalytic performance is strongly influenced by the ring substitution. Two MTO molecules coordinated to one salen ligand lead to an additional boost of catalytic activity because there is not only double the amount of catalytic
centers present but also a “ligand enhanced” activity increase.

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