Synthesis of Halfsandwich Ruthenium Complexes of Sulfinic Acid Esters [1]

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Dedicated to Prof. Dr. Dr. h.c. Max Schmidt on the occasion of his 75th birthday

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Ruthenium Complexes, Sulfur Ligands, Diastereoselective Alkylations

A series of halfsandwich ruthenium sulfinato complexes [CpRu(PR'$_3$)$_2$(SO$_2$R)] (R = Me, CH$_2$Ph, C$_2$H$_4$Ph, Ph, 4-C$_6$H$_4$Me; PR'$_3$ = PMe$_3$, 1/2 dppm) with various electronic and steric environments around the ruthenium centre, have been prepared by insertion of SO$_2$ into a ruthenium carbon bond, by a direct ligand exchange reaction, or by oxidation of thiolato complexes with 3-chloroperoxybenzoic acid. The chiral complexes [CpRu(CO)(PPh$_3$)(SO$_2$R)] (R = Me, CH$_2$Ph, Ph) were obtained similarly by oxidation of the corresponding thiolates with magnesium monoperoxyphthalate. Alkylation of the sulfinato complexes with oxonium salts [R"$_3$O]X (R" = Me, Et; X = BF$_4$, PF$_6$) gave ruthenium complexes of sulfinic acid esters, [CpRu(L)(L')(S(O)(OR")R)]X in high yields and, for the chiral complexes, up to 82% de. The esters may be detached from the metal by ligand exchange with acetonitrile. Stronger nucleophiles such as I$^-$ or SMe$^-$ dealkylate the coordinated sulfinic acid esters.