

Synthesis and Oxidation of Ruthenium Allyl Thioether Complexes Bearing Phosphite and Phosphonite Coligands [1]

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Halfsandwich ruthenium thiolate complexes bearing electron-withdrawing phosphite or phosphonite ligands were prepared from $[\text{CpRu}(\text{PPh}_3)_2(\text{SR})]$ ($\text{R} = \text{Ph}, \text{CH}_2\text{Ph}, \text{Me}$) and triphenylphosphite or (*S,S*)-bis(binaphthylphosphonito)ethane (bbpe), respectively. Reaction with 1-bromo-3-methyl-2-butene in the presence of NH_4PF_6 gave the corresponding allylthioether complexes $[\text{CpRu}(\text{PR}'_3)_2(\text{S}(\text{R})\text{CH}_2\text{CH}=\text{CMe}_2)]\text{PF}_6$. Treatment with an excess of dimethyldioxirane (DMD) transformed the triphenylphosphite derivatives into diastereomeric (oxiranylmethyl)sulfoxide complexes with 18 - 80% de. NMR monitoring of the reaction revealed that the oxidant attacks the sulfur atom and the C=C double bond with comparable rates. Similar oxidation of the bbpe complexes gave mixtures of four diastereoisomers with ratios of (64 : 15 : 13 : 8) and (51 : 24 : 15 : 10), respectively.