Cationic Ruthenium-Sulfine Complexes: Synthesis and Dynamic Behaviour [1]

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Cationic ruthenium sulfine complexes [CpRu(PR′ 3 ) 2 (O=S=CHR)]PF 6 have been obtained by a variety of methods. Oxidation of the thioaldehyde complexes [CpRu(PR′ 3 ) 2(S=CHR)]PF 6 with either 2-tosyl-3-phenyl-oxaziridine (PR′ 3 = PMe 3 ) or magnesium-monoperoxyphthalate (PR′ 3 = 1/2 dppm) gave complexes of arylsulfines (R = Ph, 3-C 6 H 4 F, 4-C 6 H 4 Cl, 4-C 6 H 4 OMe) selectively in their thermodynamically less stable E form. Siloxane elimination from the sulfinato complexes [CpRu(PMe 3 ) 2(SO 2 CHRSiMe 3 )] yielded complexes of aliphatic sulfines, [CpRu(PMe 3 ) 2(O=S=CHR)]PF 6 (R = H, Me). Treatment of [CpRu(dppm)(SO 2 CH 2 R)] with acetyl chloride led to an oxygen redistribution giving complexes of thioaldehydes [CpRu(dppm)(η 2 -S=CH 2 )]PF 6 and [CpRu(dppm)(η 1 -S=CHR)]PF 6 (R = Ph, 4-C 6 H 4 Cl). The structure of the latter was determined by X-ray crystallography. The loss of oxygen can be suppressed by performing the acylation-elimination sequence in the presence of poly-(4-vinylpyridine). This provided a selective access to complexes of Z-sulfines, [CpRu(PMe 3 ) 2(O=S=CHR)]PF 6 (R = Ph, 4-C 6 H 4 Cl) and [CpRu(dppm)(O=S=CHR)]PF 6 (R = Ph, 4-C 6 H 4 Cl, COOEt, Cl). Complexes of the parent sulfine O=S=CH 2 were also obtained by SO transfer to the methane complex [CpRu(PMe 3 ) 2(CH 2 )]PF 6 and methylene transfer to the sulfur monoxide complex [Cp*Ru(PMe 3 ) 2(SO)]PF 6. Most of the new sulfine complexes exhibit dynamic behaviour in solution, i.e., ligand rotation, ligand inversion, and η 2 / η 1 hapticity change. O-Alkylation provided the dicationic complex [CpRu(PMe 3 ) 2(EtO=S=CHMe)](PF 6 ) 2, and S-oxidation gave the sulfene complexes [(C 5 R 5 )Ru(PMe 3 ) 2(O 2 S=CH 2 )]PF 6 (R = H, Me).