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_6H_4F, 4-C_6H_4Cl, 4-C_6H_4OMe) selectively in their thermodynamically less stable *E* form. Siloxane elimination from the sulfinato complexes $[CpRu(PMe_3)_2(SO_2CHRSiMe_3)]$ yielded complexes of aliphatic sulfines, $[CpRu(PMe_3)_2(O{=}S{=}CHR)]PF_6$ (R = H, Me). Treatment of $[CpRu(dppm)(SO_2CH_2R)]$ with acetyl chloride led to an oxygen redistribution giving complexes of thioaldehydes $[CpRu(dppm)(\eta^2\text{-}S{=}CH_2)]PF_6$ and $[CpRu(dppm)(\eta^1\text{-}S{=}CHR)]PF_6$ (R = Ph, 4-C_6H_4Cl). 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_6H_4Cl) and $[CpRu(dppm)(O{=}S{=}CHR)]PF_6$ (R = Ph, 4-C_6H_4Cl, COOEt, Cl). Complexes of the parent sulfine $O{=}S{=}CH_2$ were also obtained by SO transfer to the methylene 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 $[CpRu(PMe_3)_2\ (EtO\text{-}S{=}CHMe)](PF_6)_2$, and S-oxidation gave the sulfene complexes $[(C_5R_5)Ru(PMe_3)_2\ (O_2S{=}CH_2)]PF_6$ (R = H, Me).