

Solvent effect on the oxidative addition of HS-C₆H₄Br to CpFe(dppe)⁺; a reaction involving an Fe-S intramolecular electron transfer

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The solvent effect on the oxidative addition reaction of p-Br-C₆H₄-SH to CpFe(dppe)I (dppe=Ph₂P(CH₂)₂PPh₂), was studied by UV-visible spectroscopic methods. In solvents with high dielectric constants as propanediol-1,2-carbonate, formamide and N-methylformamide the product (CpFe(dppe)-SR)PF₆ was observed, while that in most lower dielectric constants solvents as dichloromethane, chloroform, acetonitrile or dimethylsulfoxide no reaction or decompositions was observed. It was demonstrated that the solvent effect arises mainly from the Fe-I bond ionization of the CpFe(dppe)I precursor to give the reactive fragment CpFe(dppe) (solv)⁺. A probable mechanism involving the electron transfer step [CpFe^{II}(dppe)-S(H)R]⁺ ? [CpFe^{III}(dppe)-SR]⁺ is discussed.