Reactivity of [(arene)(chloro)(phosphino)ruthenium(II)]+ complexes towards thiourea nucleophiles

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Abstract

Arene Ru(II) complexes; (η^6-Benzene)chloro-*bis*(triphenylphosphino)ruthenium(II) chloride, **C1**, (η^5-cyclopentadienyl)chloro-bis(triphenylphosphino)ruthenium(II) Chloride, **C2**, (η^6-Benzene)chloro{*bis*(diphenylphosphino)methane}ruthenium(II) Chloride, **C3**, η^5-cyclopentadienyl)[*bis*(diphenylphosphino)methane]ruthenium(II), **C 4** (η^6-Benzene)chloro{1,2-*bis*(diphenylphosphino)ethane}ruthenium(II) Chloride, **C5** and (η^6-Benzene)chloro{1,3-*bis*(diphenylphosphino)propane}ruthenium(II) Chloride, **C6** were successfully synthesized by modified literature methods. The rates of chloro substitution and mechanism of reactions of the arene Ru(II) complexes by thiourea nucleophiles were studied under *pseudo* first order conditions in 0.1 M $NaClO_4$/LiCl methanol solution as a function of nucleophile concentration and temperature. The reactions were monitored using the UV–vis absorption spectrophotometer or stopped flow spectrophotometer for fast reactions. The coordinated arene ligand donates electrons towards the Ru metal ion centre and its π -electron cloud presents an electrostatic repulsive effect onto and around the Ru centre as measured by the projected cone angle. The bidentate *bis*(diphenylphosphino)methane ligand hinders the approach of nucleophiles during the substitution process. When the bis(diphenylphosphino)methane chelate is expanded through the introduction of a methylene carbon within the bridge, the steric hindrance to the approach of nucleophiles is reduced because of the trough like conformation of the alkyl chain which traps the nucleophiles within the coordination sphere. This enhances the reactivity by a factor of 10^3. The observed reactivity trends are

supported by DFT calculations. The entropy of activation values are positive indicating that the mechanism of substitution has interchange dissociative (I_D) character.