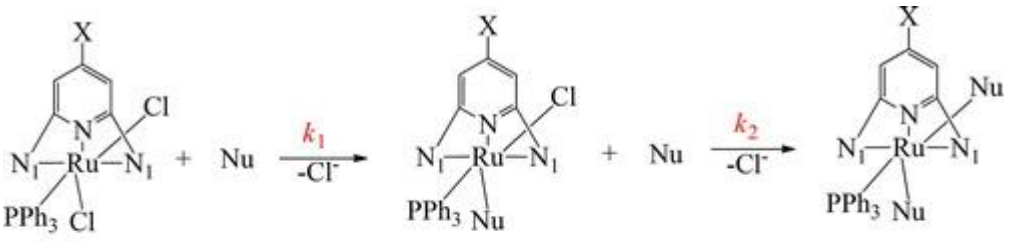
The effect of substituents on the reactivity of dichloridotriphenylphosphinoruthenium(II) complexes: kinetic and mechanistic study.

Abs

Formulae display: 2

Abstract.

The rates of substitution of chloro ligands from a series of ruthenium(II) complexes, [Ru(κ³-L)(PPh_3)Cl_2] (L = 2,2′:6′,2″-terpyridine, **1**; 4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine, **2**; 4,4′4″-tri-tert-butyl-2,2′:6′,2″-terpyridine, **3**; 4′-(4-chlorophenyl)-2,2′:6′,2″-terpyridine, **4**; 4-chloro-2,2′:6′,2″-terpyridine, **5** and 2,6-bis(2-pyrazolyl)pyridine, **6**), by thiourea nucleophiles was investigated under *pseudo*-first-order conditions in methanol as a function of nucleophile concentration and temperature. The chloro ligands were substituted in two steps and the reactivity trend was **4** > **5** > **2** > **1** > **6**. Complexes **2** and **3** having donor substituents on the 2,2′:6′,2″-terpyridine backbone experience a *trans*-effect making them more reactive than **1**. Complexes **4** and **5** are more reactive than **1** due to enhanced π-back-bonding brought about by electron-withdrawing substituents on their 2,2′:6′,2″-terpyridine backbones. The reactivity of **4** is higher than **5** due to greater electron acceptor-ability of the chlorophenyl substituent than the chloro substituent in **5**. The 2,6-*bis*(pyrazolyl)pyridine ligand in **6** retards the reactivity of the complex compared to **1** due to the *cis*-donor effect of the pyrazole. The reactivity of the complexes is associative for all nucleophiles in step one and only thiourea in step two. The substitution reactions proceed by a steady changeover from an associative interchange mechanism (I_a) to a dissociative interchange (I_d) mechanism on increasing steric hindrance.



1
X = H
N_1 = 2-Pyridyl

2
X = 4-methylphenyl
N_1 = 2-Pyridyl

3
X = tert-butyl
N_1 = 4-tert-butyl-2-pyridyl

4
X = 4-chlorophenyl
N_1 = 2-Pyridyl

5
X = chloro
N_1 = 2-Pyridyl

6
X = H
N_1 = 2-Pyrazolyl

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