

Stereospecific Substitution of the Chloro-Ligand by Acetonitrile in the Diastereomeric ($\eta^5\text{-C}_5\text{H}_5$)RuCl-[(R)-Ph₂PCH(CH₃)CH₂PPh₂]-Complexes

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The substitution of the halogen atom by neutral two-electron-donors in transition metal complexes in the presence of a halide acceptor is a common reaction in organometallic and inorganic chemistry [1].

Having structurally characterized both diastereomers [(S)_{Ru}-(R)_C]-CpRuCl(prophos) (1) and [(R)_{Ru}-(R)_C]-CpRuCl(prophos) (2) (prophos = (R)-1,2-bis-(diphenylphosphino)propane and Cp = η^5 -cyclopentadienyl) [2, 3], the determination of the stereochemistry of that reaction becomes feasible. Furthermore, once the conditions for a stereospecific reaction are found, it should be possible to investigate the influence of the chirality at the metal on steric discrimination in the case of chiral or prochiral two-electron-donors [4]. The significance of such investigations is obvious for a better understanding of the basic phenomena in homogeneous asymmetric catalysis by transition metal complexes [5].

We report here that (1) or (2) react at room temperature with acetonitrile (large excess) in methanolic solution in the presence of ammonium hexafluorophosphate to give (Scheme) (3) or (4) respectively with high stereospecificity (>95%), and with retention of configuration at the ruthenium atom.

A mixture of 0.15 g (0.25 mmol) of (1) or (2), 0.2 g (1.2 mmol) of NH₄PF₆ and 1 ml of CH₃CN was stirred in 10 ml of CH₃OH for a few hours [6, 7]. After removal of the solvent, the crude product was dissolved in CH₂Cl₂ and the solution filtered. Yellow crystals of analytically pure (3) or (4) precipitated upon addition of n-hexane. Yields were higher than 90%. The stereospecificity of the reaction, consistently higher than 95%, is clearly recognized by NMR characterization of (3) and (4).

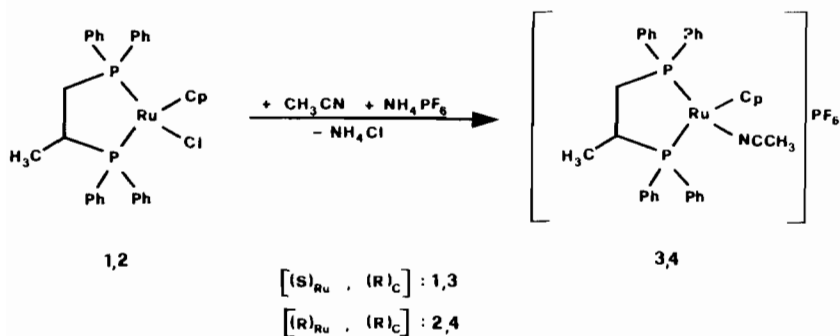
(3), ¹H-NMR (60 MHz, CD₂Cl₂): $\delta(\text{CH}_3\text{CN}) = 1.46$, $J_{\text{PH}} = 1.1$ Hz; $\delta(\text{Cp}) = 4.65$; ³¹P-NMR (24.28 MHz, CH₂Cl₂): $\delta(\text{P}_\text{A}) = 95.6$, $\delta(\text{P}_\text{B}) = 71.3$, $J_{\text{P-P}} = 32.9$ Hz. (4), ¹H-NMR: $\delta(\text{CH}_3\text{CN}) = 1.71$, $J_{\text{PH}} = 1.1$ Hz; $\delta(\text{Cp}) = 4.49$; ³¹P-NMR: $\delta(\text{P}_\text{A}) = 88.1$, $\delta(\text{P}_\text{B}) = 75.7$, $J_{\text{P-P}} = 25.6$ Hz.

The crystal structure* of (3) (Fig. 1) shows an (S) absolute configuration at the ruthenium atom, according to the accepted nomenclature [8]. Therefore, the substitution of the chloro ligand in (1) and (2) by acetonitrile has taken place with retention of the configuration.

*The [(S)_{Ru}-(R)_C]-[($\eta^5\text{-C}_5\text{H}_5$)Ru(NCCH₃)(prophos)]-[PF₆] \cdot 2CH₂Cl₂ diastereomer crystallizes in the triclinic P1 space group with $a = 11.944(2)$, $b = 10.280(2)$, $c = 9.779(2)$ Å, $\alpha = 108.44(2)$, $\beta = 63.87(2)$ and $\gamma = 103.44(2)$, $Z = 1$ and $U = 1016.5$ Å³.

The structure was solved by conventional Patterson and Fourier methods on the basis of 1418 significant reflections with $I > 3\sigma(I)$ in the range $3^\circ < \theta < 18^\circ$ (the crystals lose solvent).

The absolute configuration was determined by internal comparison. The current R and Rw values are 0.069 and 0.071, respectively.



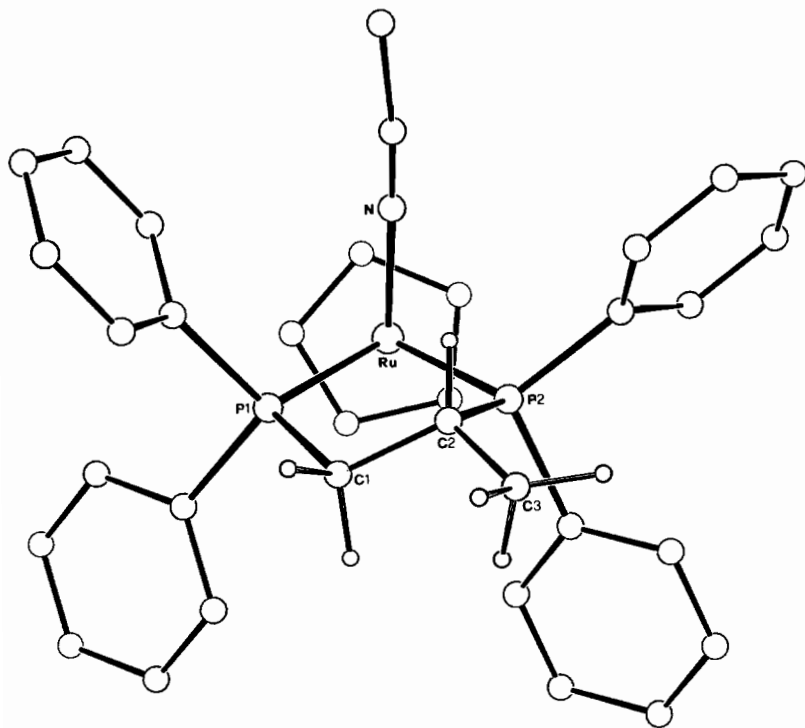


Fig. 1. View of the $[(S)_{Ru},(R)_C]-[(\eta^5-C_5H_5)Ru(NCCH_3)(prophos)]^+$ cation in its absolute configuration as determined from X-ray analysis. Relevant bond parameters are as follows: Ru-N, 2.02(2); Ru-P, 2.28 (mean); Ru-Cp, 2.2 (mean).

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