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Stereospecific Substitution of the Chloro-Ligand by Acetonitrile in the Diastereomeric (η^5-C_5H_5)RuCl-[(R)-$Ph_2PCH(CH_3)CH_2PPh_2$]-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].

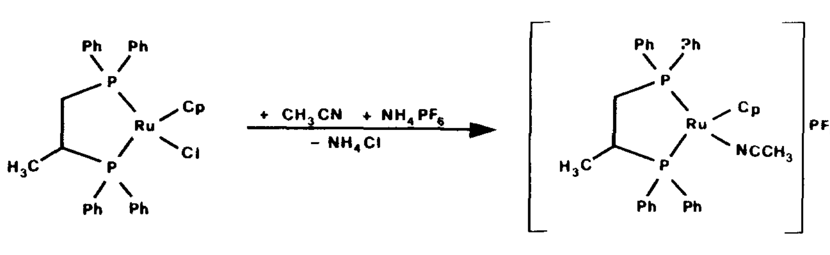
Having structurally characterized both diastereomers [$(S)_{Ru}$,$(R)_C$]-CpRuCl(prophos) (*1*) and [$(R)_{Ru}$,$(R)_C$]-CpRuCl(prophos) (*2*) (prophos = (R)-1,2-bis(diphenylphosphino)propane and Cp = η^5-cyclopentadienyl) [2, 3], the determination of the stereochemistry of that reaction becomes feasible. 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 NH_4PF_6 and 1 ml of CH_3CN was stirred in 10 ml of CH_3OH for a few hours [6, 7]. After removal of the solvent, the crude product was dissolved in CH_2Cl_2 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*), ^{1}H-NMR (60 MHz, CD_2Cl_2): $\delta(CH_3CN) = 1.46$, $J_{PH} = 1.1$ Hz; $\delta(Cp) = 4.65$; ^{31}P-NMR (24.28 MHz, CH_2Cl_2): $\delta(P_A) = 95.6$, $\delta(P_B) = 71.3$, $J_{P-P} = 32.9$ Hz. (*4*), ^{1}H-NMR: $\delta(CH_3CN) = 1.71$, $J_{PH} = 1.1$ Hz; $\delta(Cp) = 4.49$; ^{31}P-NMR: $\delta(P_A) = 88.1$, $\delta(P_B) = 75.7$, $J_{PP} = 25.6$ 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.



1,2

3,4

[$(S)_{Ru}$, $(R)_C$] : 1,3

[$(R)_{Ru}$, $(R)_C$] : 2,4

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*The [$(S)_{Ru}$,$(R)_C$]-[(η^5-C_5H_5)Ru($NCCH_3$)(prophos)]-[PF_6]·$2CH_2Cl_2$ 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 $U = 1016.5$ Å^3.

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 $3° < \theta < 18°$ (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.

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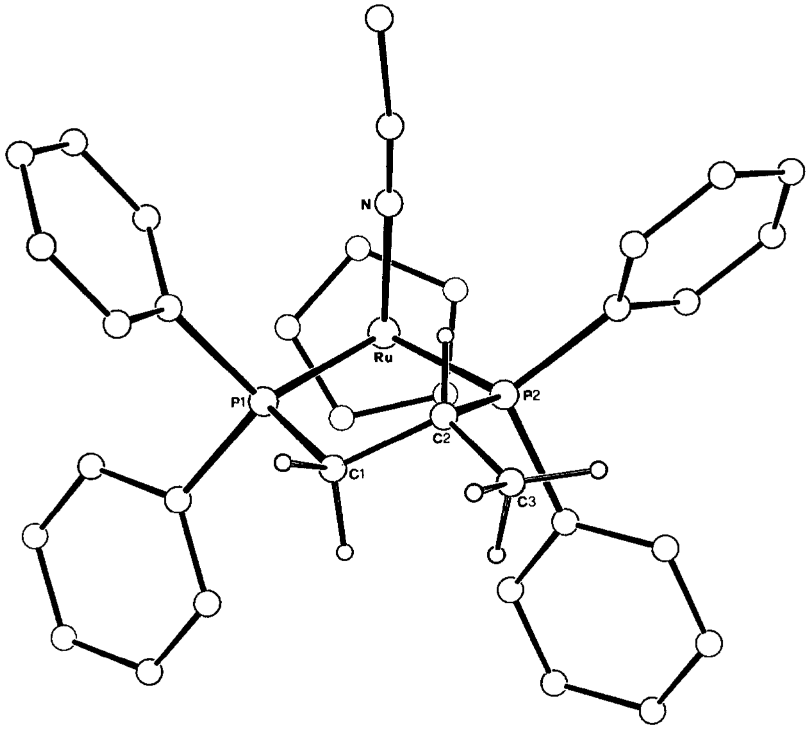

Fig. 1. View of the $[(S)_{Ru},(R)_C]$-$[(\eta^5$-$C_5H_5)Ru(NCCH_3)(prophos)]^+$ cation in its absolute configuration as determined from X-ray analysis. Relevant bond parameters are as follows: Ru–N, 2.02(2); Ru–P, 2.28 (mean); Ru–Cp, 2.2 (mean).

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