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Preliminary communication

OPTICALLY ACTIVE $[(\eta\text{-}C_5H_5)Ru\{(R)\text{-}Ph_2PCH(CH_3)CH_2PPh_2\}(Olefin)]PF_6$ COMPLEXES: INFLUENCE OF THE STEREOGENIC METAL ATOM ON THE ENANTIOFACE SELECTION

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Summary

The synthesis and characterization of optically active olefinic complexes of the type $[(\eta\text{-}C_5H_5)Ru\{Ph_2PCH(CH_3)CH_2PPh_2\}(CH_2{=}CHR'')]PF_6$ ($R'' = H$, CH_3, C_6H_5, $COOCH_3$), in which the metal is a stereogenic center, are reported. The enantioface discrimination of the prochiral olefin is influenced by the chiral ligand and by the stereogenic metal atom. The chiral center at the metal appears to be optically labile. The rates of the epimerization at the metal and of the olefin enantioface depend on the structure of the coordinated olefin.

Enantioface selection with olefinic substrates is observed in asymmetric catalytic reactions by transition metal complexes such as hydrogenation [1], hydrocarbonylation [2], isomerization [3], and stereospecific polymerization [4]. As a consequence, the enantioface discriminating complexation of olefins has received much attention, and has been investigated, both that brought about by chiral ligands [5] and that arising from chirality at the metal [6].

We present here the first examples of diastereomeric equilibria in olefinic metal complexes in which enantioface discrimination is determined simultaneously by a chiral ligand and by the chiral center at the metal, which can have the opposite absolute configuration.

Starting from diastereomerically pure $(S)_{Ru}$, $(R)_C$ – **1** and $(R)_{Ru}$, $(R)_C$-$[(\eta\text{-}C_5H_5)RuCl\{Ph_2PCH(CH_3)CH_2PPh_2\}$ (**1'**) [7] the olefin complexes were prepared (Scheme 1) by reaction in methanol at room temperature with excess of the

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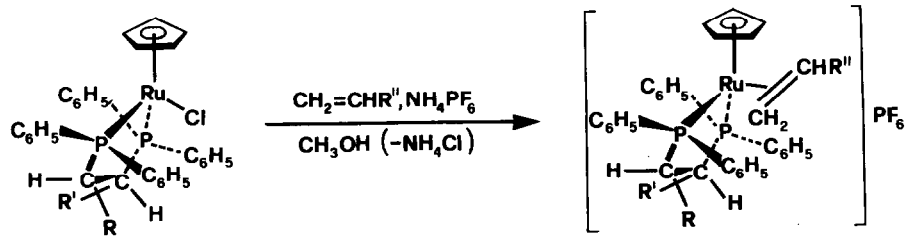


$(S)_{Ru},(R)_C$-**1** (R = CH_3, R' = H)

$(R)_{Ru},(R)_C$-**1'** (R = H, R' = CH_3)

$(S)_{Ru},(R)_C$-**2**

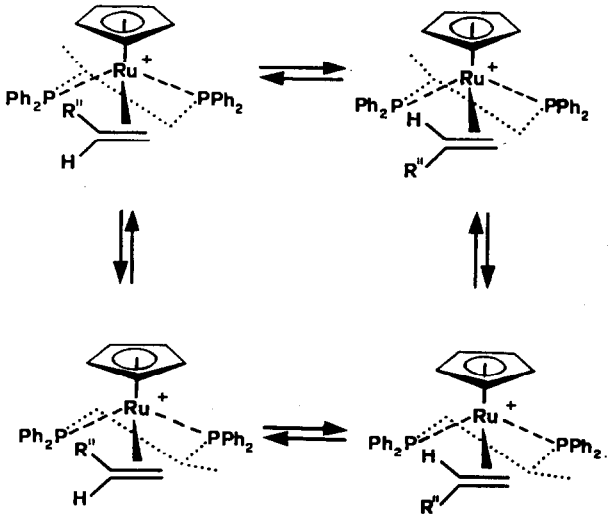
$(R)_{Ru},(R)_C$-**2'**

a, R'' = H
b, R'' = CH_3
c, R'' = C_6H_5
d, R'' = $COOCH_3$

appropriate olefin in the presence of NH_4PF_6 as halogen scavenger. After removal of the solvent under vacuum the pale-yellow complexes were obtained pure (according to elemental analysis) by recrystallization from CH_2Cl_2/n-C_6H_{14}.

The ^{31}P and ^1H NMR spectra of the ethylene complexes **2a** and **2'a** obtained from **1** and **1'**, respectively, recorded immediately after dissolution in CD_2Cl_2 show the products to have diastereomeric purities of 62 and 80%, respectively. Both solutions, when left at room temperature for ca. 4 days, reach an equilibrium **2a**/**2'a** ratio of 35/65 [8]. It thus appears that formation of **2a** and **2'a** is largely stereospecific. We assume that it takes place with retention of configuration at the metal, since this is the case when other 2e donors are involved in the substitution of the chlorine ligand in **1** and **1'** [9].

Similar behaviour is observed for the methyl acrylate derivatives **2d** and **2'd**. In this case, however, since the olefin is prochiral double the number of species are expected (Scheme 2). (Rotation of the olefin is not considered since it should be rapid at room temperature). The complexes are formed with the same relatively high



stereospecificity. The product mixture obtained from **1** can be shown immediately after dissolution to contain four species, in a 70/16/7/7 molar ratio, but the same species are formed in 18/5/30/47 ratio when **1'** is the starting material. The equilibrium composition is 22/5/19/54 and is reached after about 48 h. Diastereoface selection at equilibrium for **2d** (4.4) is therefore different from that for **2'd** (2.8) [10]. It is notable that for the analogous complexes containing the (2*S*,3*S*)-2,3-butanediylbis(diphenylphosphine) ligand, in which the metal is not stereogenic, the diastereoface selection is even lower (1.2) [11]. We have no evidence at present to identify the enantioface preferentially complexed in the two diastereomeric species **2d** and **2'd**.

The results for the complexes containing propylene **2b** and **2'b** [12] and styrene **2c** and **2'c** [13] are less sharply differentiated. Independent of which starting material is used immediately after dissolution four species are present, in a molar ratio of 59/24/7/10 for the propylene complexes and a molar ratio of 53/25/18/4 for the styrene complexes. These ratios do not change with time. Even an incomplete stereochemical assignment is therefore impossible in this case, probably owing to a very rapid epimerization at the olefin prochiral face and at the ruthenium atom.

Although the stereochemical identification of all the diastereomeric species in solution is not yet possible, the reported results show for the first time that the nature of the stereogenic metal atoms (as well as that of the chiral ligands) can be important in determining the steric discrimination involving prochiral olefinic ligands at thermodynamic equilibrium.

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8 **2a** ^{1}H NMR: $\delta(C_5H_5)$ 5.03 s. ^{31}P NMR (δ from H_3PO_4): 88.2 and 61.9 (d, J(PP) 31.1 Hz).
2'a ^{1}H NMR: $\delta(C_5H_5)$ 4.43 s. ^{31}P NMR (δ from H_3PO_4): 82.4 and 58.9 (d, J(PP) 38.5 Hz).
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10 **2d**. ^{1}H NMR: $\delta(C_5H_5)$ 5.01 s and 4.89; $\delta(OCH_3)$ 3.01 s and 3.77. ^{31}P NMR (δ from H_3PO): 84.3 and 62.5 (d, J(PP) 31.7 Hz); 84.8 and 59.2 (d, J(PP) 31.7 Hz).
2'd ^{1}H NMR: $\delta(C_5H_5)$ 4.43 s and 4.30; $\delta(OCH_3)$ 3.43 s and 3.68. ^{31}P NMR (δ from H_3PO_4): 85.2 and 49.6 (d, J(PP) 36.6 Hz); 80.3 and 53.2 (d, J(PP) 36.6 Hz).
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12 **2b,2'b** ^{1}H NMR: $\delta(C_5H_5)$ 4.85 s, 4.52, 4.22 and 3.84; $\delta(CH_3)$ 0.57 d (J(HH) 6.3 Hz). ^{31}P NMR (δ from H_3PO_4): 88.3 and 60.7 (d, J(PP) 37.7 Hz); 81.6 and 52.5 (d, J(PP) 39.1 Hz); 84.0 and 61.6 (d, J(PP) 34.2 Hz); 81.6 and 56.3 (d, J(PP) 39.1 Hz) ppm.
13 **2c,2'c** ^{1}H NMR: $\delta(C_5H_5)$ 4.53 s, 4.49, 4.45 and 3.85. ^{31}P NMR (δ from H_3PO_4): 84.4 and 65.8 (d, J(PP) 29.3 Hz); 76.6 and 57.6 (d, J(PP) 36.6 Hz); 88.5 and 57.4 (d, J(PP) 31.7 Hz); 81.5 and 52.3 (d, J(PP) 39.1 Hz).