Diastereoselective π-Complexation: Reaction of Planar-chiral Cyclopentadienyl-Ruthenium Complexes with Prochiral Arenes

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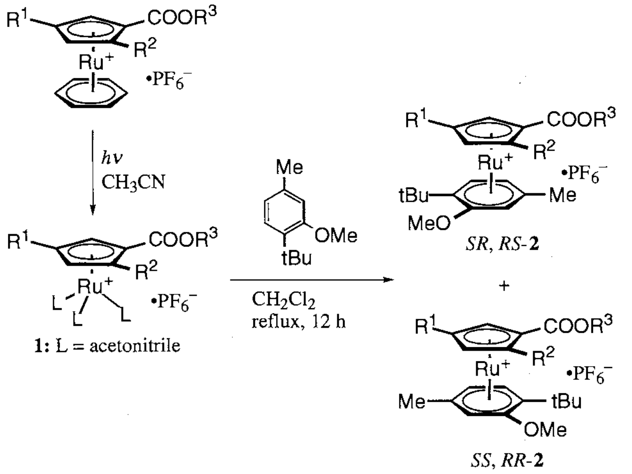
The reaction of (trisubstituted cyclopentadienyl)tris(acetonitrile)ruthenium complexes, $[Cp'Ru(CH_3CN)_3][PF_6]$, with prochiral trisubstituted arenes gave planar-chiral $[Cp'Ru(arene)][PF_6]$ complexes with a diastereoselectivity up to 46% d. e.

Cyclopentadienyl-ruthenium complex-catalyzed condensation reactions between alkynes and alkenes are currently the subject of intense interest in terms of new methods for organic syntheses.[1] In most of the reported reactions, non-substituted cyclopentadienyl- or pentamethylcyclopentadienyl-ruthenium complexes have been used as a catalyst. Recently, we have reported the synthesis of novel (η^5-trisubstituted cyclopentadienyl)ruthenium complexes $[Cp'Ru(CH_3CN)_3][PF_6]$ having a planar chirality[2] as well as the catalysis in the cyclopropanation reaction of norbornene with propargyl alcohol.[3] In the course of our study, we have examined the potentials of the planar-chiral cationic complexes $[Cp'Ru(CH_3CN)_3]^+$ for enantioselective reactions and found a through-space chiral transfer in the reaction of the complexes. Here we report diastereoselective π-complexation of planar-chiral cyclopentadienyl ruthenium species toward prochiral trisubstituted arenes.

In metal-catalyzed asymmetric reactions, enantioselective π-complexation of unsaturated hydrocarbon substrates on a chiral metal center is a key step. Several studies on the stereoselective π-complexation of unsaturated hydrocarbons have appeared, however, well-characterized examples of this process are still rare.[4]



Scheme 1.

Planar-chiral $[Cp'Ru(CH_3CN)_3][PF_6]$ **1** was prepared by the reported method (Scheme 1).[2] It is well-known that cationic $[CpRu(CH_3CN)_3]^+$ complexes undergo thermal replacement of the acetonitrile ligands by various arenes to give $[CpRu(arene)]^+$.[2,5] In order to obtain some information on the diastereoselective π-complexation of the planar-chiral Cp'Ru moiety to prochiral arenes, the reactions of complex **1a** with some kinds of prochiral arenes were carried out. The reaction of prochiral arenes with planar-chiral Cp'Ru complexes would produce $[Cp'Ru(arene)]^+$ complexes which contain two planar-chiral parts; one is the Cp'-Ru part and the other is the arene-Ru one. Thus complex **1a** was allowed to react with various arenes in dichloromethane at room temperature under nitrogen atmosphere for 12 h. Purification by column chromatography on alumina gave $[Cp'Ru(arene)]PF_6$ **2** as a mixture of two enantiomer pairs, (*SS, RR*) and (*SR, RS*).[6] In the reaction of **1a** with 2-t-butyl-5-methylanisole, asymmetric induction was observed, though it was not detected with arenes such as methyl 2-methoxybenzoate and α-tetralon.

Then, the investigation of asymmetric induction by planar-chirality on the Cp'Ru moiety was started with using 2-t-butyl-5-methylanisole as a prochiral arene. Results are summarized in Table 1. Complexes **1a**, **1d**, and **1f** showed almost the same diastereoselectivity, implying that the bulkiness of substituent R^1 at 4-position is not influential in the asymmetric induction. Complexes **1c** and **1e** bearing an ethoxy group at 2-position gave product **2** in moderate yield with a lower selectivity than **1a**. Cyclohexyl ester derivative **1b** afforded product **2b** with the highest selectivity, while cyclohexyl ester analogue **1g** having a t-Bu group at 4-position of the Cp' ligand showed a lower selectivity than **1b**, suggesting that the bulkiness of the substituent at 1-position plays an important role for the asymmetric reaction.

Table 1. Reaction of complex 1 with 2-t-butyl-5-methylanisole

Complex	R^1	R^2	R^3	Yield of **2** /% [a]	D.e. of **2** / % [b]
1a	Me	Me	Et	98	37
1b	Me	Me	Cy [c]	75	46
1c	Me	OEt	Et	43	26
1d	Ph	Me	Et	98	38
1e	Ph	OEt	Et	52	22
1f	t-Bu	Me	Et	64	37
1g	t-Bu	Me	Cy	39	19

[a] Isolated yield. [b] Determined by HPLC. [c] Cy = cyclohexyl.

The molecular structure of product **2** must aid us in understanding the mechanism of through-space chiral transfer found in the present π-complexation reaction. The fractional recrystalization of **2g** from ethanol gave the major diastereomer as a single crystal. The molecular structure of the major diastereomer was established by x-ray crystallographic analysis[7] and the stereochemistry was determined to be a pair of *RS* and

SR, indicating that the planar chirality *S* on the Cp'-Ru part induces the planar-chirality *R* on the arene-Ru part in the ligand exchange reaction. (Figure 1) The mechanism of the ligand exchange reaction of $[CpRu(CH_3CN)_3]PF_6$ with arenes was investigated in detail by Mann et. al. (eq. 1)[8] On the basis of their proposed mechanism, the reaction proceeds step by step and the last step (from **4** to **2** in eq. 1) is irreversible in CH_2Cl_2 under thermal reaction conditions. In addition, they concluded that hapticity change from η^4 in **4** to η^6 in **2** is a rate-determining step. Therefore the recognition of prochiral plane is thermally controlled by the planar-chiral Cp'-Ru moiety on the formation of the η^4 intermediate and the structure of the η^4 intermediate must be important for understanding the mechanism of the prochiral-plane recognition. On the basis of the steric repulsion between the Cp' ligand and 2-t-butyl-5-methylanisole, the Cp'RuL moiety may coordinate by using 2, 3, 4, and 5 positions on 2-t-butyl-5-methylanisole to make η^4 intermediate. (eq. 2) Then four structural isomers may be considered for the η^4-arene-Ru intermediate. (Figure 2)

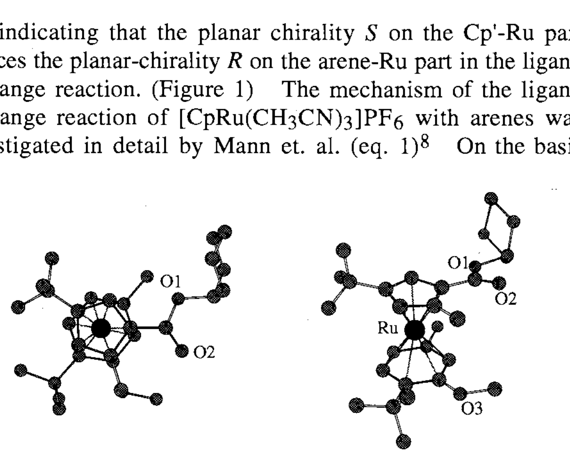
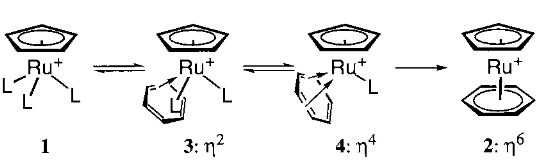
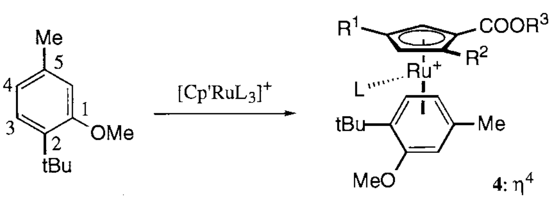


Figure 1. Molecular structure of the major diastereomer of **2g**.



(eq. 1)



(eq. 2)

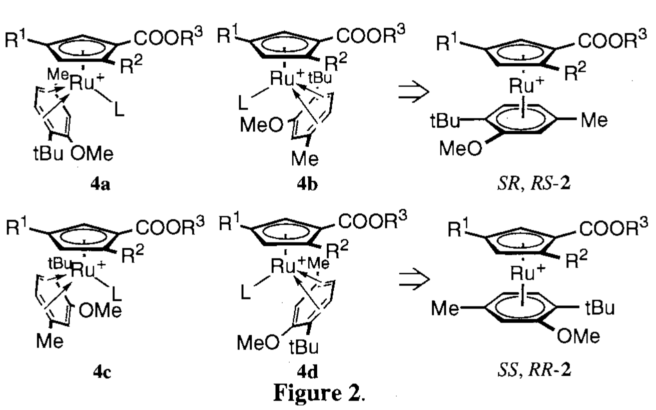


Figure 2.

Isomers **4a** and **4b** produce a diastereomer having a pair of *SR* and *RS* stereochemistry. The thermal stability of η^4-intermediates decreases in the order of **4a** > **4c** ≈ **4d** > **4b** depending on sterical repulsion between the substituentes on Cp' and η^4-arene ligands. Consequently, we propose that the present diastereoselective ligand exchange reaction preferentially passes through intermediate **4a**. According to the proposed mechanism described above, complex **1** bearing a large substituent on an ester group must exhibit a high diastereoselectivity on the π-complexation reaction of prochiral arenes. In fact, the reaction of cyclohexyl derivatives **1b** shows 46% d.e.

The work described here demonstrates the first effective transfer of a planar chirality from Cp'-Ru part to the chirality of arene-Ru complexation. The chiral recognition property of cationic planar-chiral $[CpRu(CH_3CN)_3]^+$ complexes must be useful for the design of enantioselective catalytic reactions.

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References and Note

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6 All the new compounds were characterized by IR and NMR spectroscopies and elemental analyses. Selected data, **1a**, m.p. 98 - 102°C (decomp.); IR (KBr), 1708, 1223 cm^{-1}; ^1H NMR (270 MHz, acetone-d_6) δ = 4.66 (s, 1H), 4.22 (dq, 1H, J = 3.0, 7.3 Hz), 4.19 (dq, 1H, J = 3.0, 7.3 Hz), 2.55 (s, 9H), 1.97 (s, 3H), 1.77 (s, 3H), 1.30 (t, 3H, J = 7.3 Hz). **2b**, colorless oil. IR (KBr), 1715, 1231 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ = 6.30 ~ 5.40 (m, 10H), 4.92 ~ 4.86 (m, 2H), 3.91 (s, 3H), 3.86 (s, 3H), 2.30 ~ 1.20 (m, 38H), 1.39 (s, 9H), 1.26 (s, 9H); Mass (FAB), m/z 499 (M^+–PF_6).

7 Crystal data of **2g**, $C_{29}H_{43}O_3RuPF_6$, M = 685.69 monoclinic, space group $P2_1/a$, a = 16.450(4), b = 11.284(2), c = 18.077(2) Å, β = 115.27(1)°, V = 3034.4(9) $Å^3$, z = 4, D_c = 1.501 g cm^{-3}, μ(MoKα) = 6.35 cm^{-1}, T = 203 K. The data was collected using a RIGAKU AFC-5R diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å) by the ω-2θ scan method in the range 5 < 2θ < 50. 5848 measured reflections, 5643 unique reflections, 3996 reflections with I ≥ 3σ(I) were used in refinment, empirical absorption correction (ψ-scan), *R* = 0.060, R_W = 0.068. The structure was solved by Paterson method in the teXsan crystallographic software package of Molecular Structure Corporation and refined anisotoropically for non-hydrogen atoms. Hydrogen atoms were placed in appropriate trigonal or tetrahedral positions.

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