Synthesis and Property of Planar-chiral Cyclopentadienyl-ruthenium Complexes

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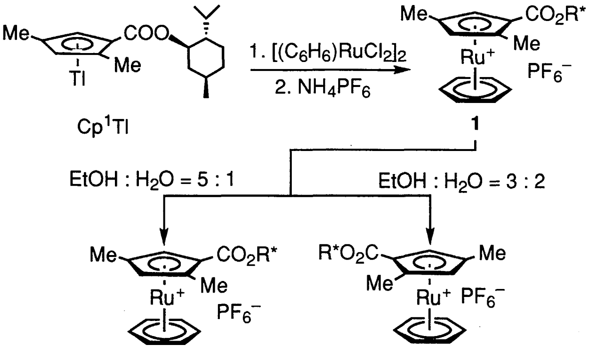
The first enantiomerically pure planar-chiral cyclopentadienyl-ruthenium complexes, [Cp^{n}Ru(benzene)]PF$_6$, were synthesized (Cp^{n}H; unsymmetricaly trisubstituted cyclopentadiene), and by a photo reaction with CH$_3$CN converted to [Cp^{n}Ru(CH$_3$CN)$_3$]PF$_6$, which was transformed into planar-chiral [Cp^{n}Ru(arene)]PF$_6$ by a ligand exchange reaction.

Cyclopentadienyl-metal complexes have wide application in organic syntheses.[1] Recently, cyclopentadienyl-ruthenium complexes have attracted much attention in terms of novel catalytic properties on the C-C bond formation and [4+2]cycloaddition reaction.[2] In most of reports about these reactions, non-substituted cyclopentadienyl- or pentamethylcyclopentadienyl-ruthenium complexes have been used, and because of luck of the suitable synthetic method, chiral cyclopentadienyl-ruthenium complexes have not been known so far except stable ruthenocene derivatives.[3] Previously, we have reported a new method for the synthesis of enantiomerically pure planar-chiral cyclopentadienyl complexes of Fe[4], Rh[4] and Co[5, 6] by the use of a trisubstituted cyclopentadiene (Cp^{1}H) having a removable chiral auxiliary, (−)-menthyl group. Here, we report the first synthesis of planar-chiral cyclopentadienyl(η^6-benzene)ruthenium complex, [Cp^{1}Ru(benzene)]$^+$. The complex is readily converted to [Cp^{1}Ru(CH$_3$CN)$_3$]$^+$ by a photo reaction with acetonitrile,[7] and we may expect that lability of the acetonitrile ligands in the complex leads to a ready formation of coordinatively unsaturated CpRu$^+$ speceis having a planar-chirality.



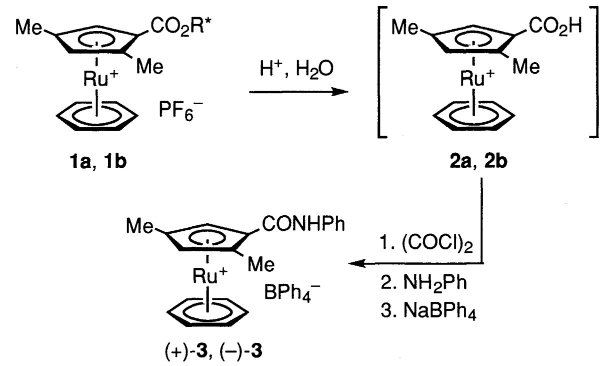
Scheme 1. Synthesis of diastereomers.

Table 1. Synthesis of planar-chiral [Cp^{1}Ru(C$_6$H$_6$)]PF$_6$

Product	Yield(%)[a]	[α]^{15}$_D$ (deg.) (in CHCl$_3$)
1a+1b	50 (**1a**:**1b**=1:1)[b]	
1a	13	+3 (c 0.222)
1b	2	−54.7 (c 0.220)

[a] Isolated yield based on ruthenium source. [b] Ratio was determined by HPLC.

For the synthesis of a planar-chiral cyclopentadienyl-ruthenium complex, we used trisubstituted cyclopentadienyl-thallium (Cp^{1}Tl). The reaction of [(C$_6$H$_6$)RuCl$_2$]$_2$ with Cp^{1}Tl in acetonitrile at room temperature gave planar-chiral [Cp^{1}Ru(benzene)]X,[8] which was isolated as hexafluorophosphate **1** after purification by column chromatography on alumina and recrystallization from ethanol (Scheme 1). ^{1}H NMR and HPLC (ODS column, methanol-water) analyses showed that thus obtained [Cp^{1}Ru(benzene)]PF$_6$ consists of two diastereomers **1a** and **1b** with a ratio of 1 : 1. Separation of diastereomer **1a** from **1b** was accomplished by fractional crystallization. Pure **1a** was isolated by recrystallization from ethanol-water (5/1), while pure **1b** from ethanol-water (3/2). Analytically pure **1a** was easily obtained by recrystallization for three times but several times were needed to obtain pure **1b**. Isolated yields are summarized in Table 1 along with [α]$_D$ values of the diastereomers.



Scheme 2. Synthesis of enantiomers.

Table 2. Physical date of enantiomers **3**

Complex	mp (°C) (dec.)	[α]^{13}$_D$ (deg.) (in CH$_3$CN)
(+)-**3**	214.0-215.0	+38 (c 0.31)
(−)-**3**	213.0-214.5	−37 (c 0.26)

Conversion of the diastereomeric complexes into enantiomeric ones was carried out by hydrolysis of the chiral ester group on the cyclopentadienyl ligand. Thus, the chiral auxiliary, (−)-menthyl group, of diastereomeric complex **1a** was removed by hydrolysis in an aqueous solution of HCl,[5] and we obtained enantiomer **2a** as a carboxylic acid, however which was not isolated as a pure form. Therefore, **2a** was transformed to an acid chloride by treatment with oxaryl chloride, and then converted into anilide (+)-**3** by condensation with aniline. Similarly, enantiomer (−)-**3** was obtained from **1b**. Thus, (+)- and (−)-**3** were isolated as an enantiomerically pure form, which showed the same decompose points and absolute values of [α]$_D$ (Scheme 2, Table 2).

To establish the absolute configuration of the complexes, we carried out an X-ray structural analysis for **1a**.[9] Figure 1 depicts an ORTEP drawing of the molecular structure of **1a**. The bond distances and angles found in **1a** are essentially similar to those found in $[(CpRu)_2(\mu\text{-}C_6H_5C_6H_5)](PF_6)_2$.[10] The absolute configuration of **1a** around the Cp^1-Ru moiety has been determined to be *S* based on the configuration of the (–)-menthyl group. Complex (+)-**3** derived from **1a**, therefore, must possess *S* stereochemistry, while **1b** has the *R* configuration.

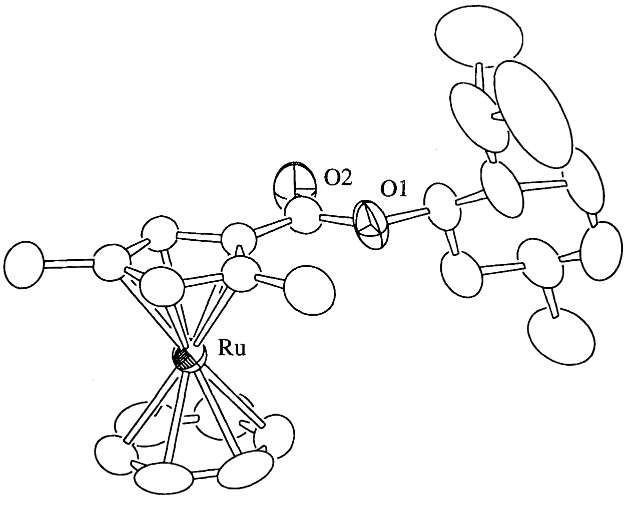
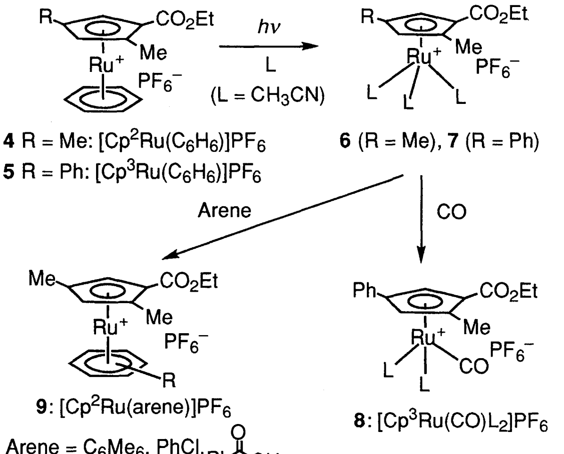


Figure 1 ORTEP drawing of **1a**. Hydrogen atoms and PF_6 are omitted for clarity.



Scheme 3. Reaction of $[Cp^nRu(C_6H_6)]PF_6$

The reaction of $[(\eta^5\text{-}C_5H_5)Ru(benzene)]X$ have been well-studied,[11] for example, the complex is easily converted to a reactive species, $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]X$ by a photo reaction, which undergoes ligand exchange reaction with several electron donors.[7] Thus, we reacted $[Cp^2Ru(benzene)]PF_6$ **4** with acetonitrile under irradiation and obtained planar-chiral $[Cp^2Ru(CH_3CN)_3]PF_6$ **6** in a quantitative yield (Scheme 3). $[Cp^3Ru(benzene)]PF_6$ **5** having a rather large substituent, phenyl, on the cyclopentadienyl ligand underwent the same exchange reaction, giving planar-chiral $[Cp^3Ru(CH_3CN)_3]PF_6$ **7**. Treatment of **7** with carbon monoxide at room temperature gave a mono-substituted product, $[Cp^3Ru(CO)(CH_3CN)_2]PF_6$ **8** in 95% yield. The exchange reaction with arenes such as hexamethylbenzene, chlorobenzene and acetophenone in dichloromethane under reflux occurred smoothly to produce planar-chiral arene complexes $[Cp^2Ru(arene)]PF_6$ **9** in a good yield. The photo reaction of diastereomerically pure **1a** in acetonitrile, followed by ligand exchange with benzene gave again **1a** without detectable change in optical purity, indicating that no racemization process of Cp'-Ru moiety is involved in the photo reaction.

These reactions of **4** and **5** suggest that the trisubstituted-cyclopoentadienyl-ruthenium complexes show almost the same reactivity as non-substituted one for the above exchange reactions. Facile replacement of the acetonitrile ligands on the central ruthenium metal may lead to potentials of planer-chiral cyclopentadienyl-ruthenium complexes in the use for asymmetric reactions.

References and Notes

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9 Crystal data for **1a**: $C_{24}H_{33}O_2F_6PRu$, M = 599.56, crystal dimensions 0.25 x 0.15 x 0.25 mm, monoclinic, space groupe $P2_1$, $a = 7.159(3)$, $b = 15.906(1)$, $c = 11.792(2)$ Å, $\beta = 97.41(2)°$, $V = 1331.6(5)$ Å^3, $Z = 2$, $D_c = 1.495$ g cm^{-3}, Mo-Kα (graphite monochromated) radiation with $\lambda = 0.7107$ Å, μ(Mo-Kα) = 7.09 cm^{-1}. 4024 reflections were collected at 20 °C on a Rigaku AFC-5FOS four-circle diffractometer in the ω-2θ scan mode with $2\theta_{max} = 60°$. The structure was solved by Patterson techniques and refined by full-matrix least squares to give $R = 0.037$, $R_W = 0.038$ for 3222 independent reflections $[F > 5\sigma(F)]$.

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12 The new compounds (**1**, **3**-**9**) were characterized by elemental analyses and IR, ^1H NMR, and Mass Spectra. Selected data for (+)-**3**, Mp 214.5 - 215.0 °C; ^1H NMR (270 MHz, acetone-d_6) δ 9.37 (s, 1H), 7.70 (d, 2H, J = 7.6 Hz), 7.40 - 7.31 (m, 10H), 7.17 (t, 1H, J = 7.6 Hz), 6.93 (t, 8H, J = 7.3 Hz), 6.78 (t, 4H, J = 7.3 Hz), 6.35 (s, 6H), 6.06 (d, 1H, J = 1.3 Hz), 5.71 (d, 1H, J = 1.3 Hz), 2.33 (s, 3H), 2.10 (s, 3H); Mass (FAB) *m/z* 392 (M^+-BPh_4).