Enantioface-Selective Complexation of Prochiral Dienes on Planar-Chiral Cyclopentadienylruthenium Complexes Bearing an Anchor Phosphine Ligand

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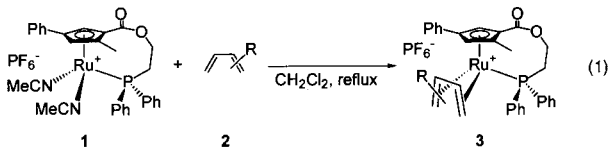
Planar-chiral cyclopentadienylruthenium complex **1** [{η^5:η^1-C_5H_2-2-Me-4-Ph-1-$CO_2CH_2CH_2PPh_2$}Ru($CH_3CN)_2$][PF_6] bearing an anchor phosphine ligand exhibits a high enantioface selectivity in the reaction with prochiral dienes **2** to give planar-chiral η^4-diene complex **3**.

Planar chirality arises from the enantioface selection of prochiral π-ligands with no C_2 axis of symmetry on coordination to a metal and thus is characteristic of organometallic π-complexes.[1,2] In the transition metal-mediated and -catalyzed asymmetric reactions of prochiral unsaturated substrates, the enantioselectivity of reactions essentially depends on enantioface selection by chiral metal species toward the prochiral substrates such as olefins and carbonyl compounds.[3] For the development of new asymmetric reactions fundamental information on enantioface selection by metal complexes is of prime importance. The enantioface selection is governed by an asymmetric environment around a metal center which lies in a metal-centered, planar or ligand chirality. Enantioselective π-complexation of unsaturated substrates has extensively been studied on metal complexes with a metal-centered[1b] and ligand chirality,[1b,4] however few studies have been made so far on effective enantioface selection by planar-chiral metal complexes.[5] Recently we have reported the synthesis of planar-chiral (η^5:η^1-cyclopentadienyl-phosphine)ruthenium complex **1** which bears a phosphine ligand as an anchor.[6] It is well-known that cationic (π-cyclopentadienyl)ruthenium complexes [π-CpRuL($CH_3CN)_2$]$^+$ (L = CO, PR_3 etc.) undergo easy replacement of the acetonitrile ligand by various dienes to give η^4-diene–ruthenium complexes [π-CpRuL(η^4-diene)]$^+$.[7] Now we have attempted to appraise the ability of our planar-chiral Ru complex [(Cp'-P)Ru($CH_3CN)_2$]$^+$ **1**[6] for enanitoface selection on diene complexation (Eq 1).



As a prochiral diene we chose isoprene and evaluated the diastereoselectivity of the reaction with complex **1**. Thus, to a dichloromethane solution of **1** was added 10 equiv of isoprene and refluxed for 12 h to give isoprene complex **3a**[8] as a mixture of diastereomers **3a-1** (major) and **3a-2** (minor) in a good yield. **3a-1** was fully characterized by spectral analyses including H-NOE spectra (*vide infra*), and finally the stereostructure has been established by an X-ray crystallographic analysis[9] to be (S_{Cp},R_{Ru},R_{diene}) or (R_{Cp},S_{Ru},S_{diene}).[10] The parent moiety {(η^5:η^1-C_5H_2-2-Me-4-Ph-1-$CO_2CH_2CH_2PPh_2$)Ru} possesses essentially the same configuration with the almost same bond distances and angles as those of an analog, [{η^5:η^1-C_5H_2-2-Me-4-Ph-1-$CO_2CH_2CH_2PPh_2$}Ru(S_2CNMe_2)][PF_6], which previously we crystallographically characterized.[6] The ORTEP diagram (Figure 1) of **3a-1** reveals that the isoprene ligand coordinates to the ruthenium center in a prone fashion[11] and bond distances and angles are in the range of those for the known η^4-diene-ruthenium complexes.[7b,12] The methyl group of isoprene ligand is located under the hydrogen at 3-position of Cp' ligand, and H^3 is under the phenyl group at 4-position (Figure 2).

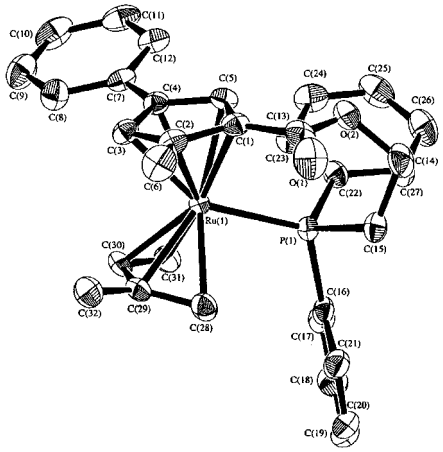


Figure 1. ORTEP drawing for **3a-1**. Selected bond distances (Å): Ru(1)-C(28) 2.227(3), Ru(1)-C(29) 2.208(3), Ru(1)-C(30) 2.173(3), Ru(1)-C(31) 2.235(3), C(28)-C(29) 1.399(4), C(29)-C(30) 1.427(5), C(30)-C(31) 1.411(5).

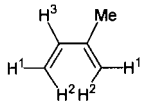


Figure 2.

Since **3a** is a product from the reaction of a racemic mixture of (S_{Cp})- and (R_{Cp})-**1**, and has three chiral centers (planar chiralities of Cp' and isoprene, and Ru-centered chirality), there should be eight possible stereoisomeres, i.e., four each for two conformers in which isoprene coordinates on Ru in a prone and supine fashion.[11] The spectral and X-ray analyses showed **3a** to adopt a prone coordination of isoprene; therefore possible isomers for **3a** are (*SRR*), (*RSS*), (*SSS*), and (*RRR*).[10] Enantioface selectivity of **1** toward isoprene may be appraised based on the ratio of diastereomers (*SRR*,*RSS*)-**3a-1**/(*SSS*,*RRR*)-**3a-2** in product **3a** (Figure 3). Thus, the P-NMR of **3a** showed two singlets at δ 52.95 and 51.52 with an integral ratio of 12.5 : 1. H-NMR of **3a** also showed two sets of signals, indicating the formation of two diastereoisomers **3a-1** and **3a-2**. The integral ratios of the two isomers in the P- and H-NMR spectra suggest a high

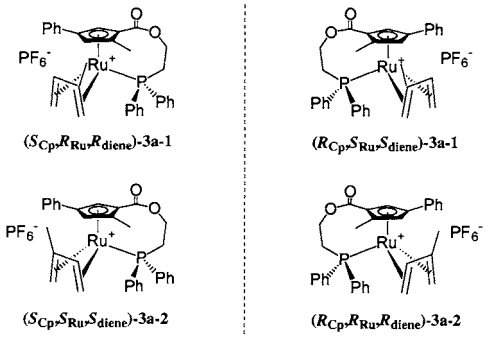


Figure 3. Stereomers of **3a**.

enantioface selection of 12.5/1 (86% d.e.) on the coordination of isoprene to **1**.

H-NOE spectra for **3a** clearly revealed an interaction of the methyl group of isoprene with the methyl at 2-position as well as with the proton at 3-position of Cp' ligand, suggesting a prone coordination of the isoprene ligand in **3a**. This stereochemistry accords with that established by the X-ray analysis, indicating the same stereostructure both in solids and in a solution. The NMR study also indicated that even in a solution the coordination of isoprene is fairly strong enough to restrict its dissociation and rotation leading to epimerization at least at ambient temperature.

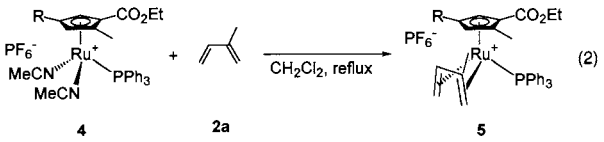
Taking account of the steric effects of substituents on the planar-chiral cyclopentadienyl and isoprene ligands, the enantioface selection toward isoprene by **1** is likely to be controlled by the asymmetric environment constructed by the planar chirality of Cp'. Difference in steric bulkiness between hydrogen and phenyl group on the Cp' ligand seems to be suitable for discriminating the enantioface of isoprene which results in the predominant formation of complex **3a-1** with a configuration of (*SRR*) or (*RSS*).

Table 1. Enantioface selectivity toward prochiral dienes

Entry	Diene **2**	**3**	
		d.e.[a] / %	yield[b] / %
1	isoprene	86	90
2	1,3-pentadiene	36	86
3	1,3-hexadiene	36	88
4	2,4-Hexadien-1-ol	18	87

[a]Determined by ^{31}P-NMR analyses. [b]Isolated yields.

The enantioface selectivity of complex **1** was also examined toward other dienes, and **1** was allowed to react with several prochiral dienes **2** under the same conditions (Table 1). Complex **1** exhibited a selectivity toward dienes such as *trans*-1,3-pentadiene and *trans*-1,3-hexadiene, but the selectivity is lower than that for isoprene. A low selectivity was observed toward 2,4-hexadien-1-ol. These observations suggest that large difference in the steric bulkiness of substituents on prochiral dienes should be required for high enantioface selection by **1**. Particularly the substituent at 2-position on dienes is likely recognized by the planar-chiral Cp' ligand with an assist from the two phenyl groups of the anchor phosphine ligand,[13] since complex **4** bearing no anchor ligand, thus the Cp' ligand is allowed to rotate around the bonding axis, showed a lower selectivity of 44% d.e. on treatment with isoprene (Eq 2), indicating an important role of the anchor phosphine ligand for enantioface-selective complexation of dienes.



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8 IR (KBr) 1727 (C=O) cm^{-1}. MS (FAB) *m/z* 581. Found: C, 52.74; H, 4.25%. Calcd for $C_{32}H_{32}F_6O_2P_2Ru$: C, 52.97; H, 4.45%. **3a-1:** ^{1}H-NMR (acetone-d_6, 400 MHz) δ 7.78–7.57 (m, 10H, Ph), 7.41–7.32 (m, 3H, Ph), 7.07 (br, 2H, Ph), 6.30 (d, 1H, *J* = 1.0 Hz, CpH), 5.82–5.76 (m, 2H, H^3, CpH), 5.33–5.22 (m, 1H, OCH_2), 4.49 (ddt, 1H, *J* = 2.2, 5.6, 11.7 Hz, OCH_2), 3.53–3.36 (m, 3H, PCH_2, H^1), 3.32 (s, 1H, H^1), 2.58 (s, 3H, Me), 2.30 (d, 3H, *J* = 1.5 Hz, Me), –0.17 (dd, 1H, *J* = 2.0, 16.1 Hz, H^2), –0.29 (ddd, 1H, *J* = 2.2, 9.5, 15.9 Hz, H^2) ppm. ^{31}P-NMR (acetone-d_6, 160 MHz) δ 52.95. **3a-2:** ^{31}P-NMR (acetone-d_6, 160 MHz) δ 51.52.

9 Crystal data for **3a-1**·CH_3COCH_3: $C_{38}H_{44}F_6O_4P_2Ru$, FW = 841.77, triclinic, space group $P\bar{1}$(#2), *a* = 12.548(3), *b* = 14.590(3), *c* = 11.140(2) Å, α = 107.23(1), β = 111.85(1), γ = 70.55(2)°, *V* = 1750.1(6) Å^3, *Z* = 2, d_{calcd} = 1.597 g·cm^{-3}, μ = 6.13 cm^{-1}, *R* (R_w) = 0.067 (0.110) for 460 parameters against 7370 reflections with $I > 3.0\,\sigma(I)$ out of 8423 unique reflections by full-matrix least-squares method, GOF = 1.14. The structure was solved and refined with teXsan program package.

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