Diastereoselective Oxidative Addition of Allyl Chloride to Planar-Chiral Cyclopentadienyl−Ruthenium Complexes

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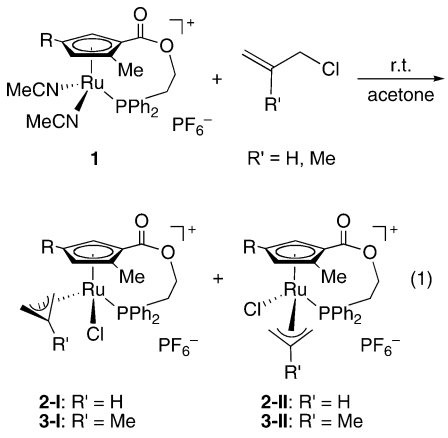
Summary: The reaction of planar-chiral cyclopentadienyl−ruthenium complexes with allyl chloride at room temperature resulted in the diastereoselective formation of π-allyl−ruthenium complexes, in which the chirality at the Ru center depended on the substituent at the 4-position of the cyclopentadienyl group. Epimerization at the Ru center of π-allyl complexes at 90 °C suggested that the diastereoselectivity was under kinetic control.

Enantioselective allylic substitution is a representative asymmetric reaction catalyzed by transition-metal complexes because of its high productivity and application in the total synthesis of a variety of biologically important molecules.[1] Although Pd-based catalysts have been widely used in enantioselective allylic substitution, recent studies have shown that other transition metals can be used with efficiencies similar to or better than those of Pd catalysts.[2,3] Recently, we reported the first example of Ru-catalyzed asymmetric allylic substitution by using planar-chiral cyclopentadienyl (Cp′) complexes.[4] To obtain more information on the origin of the enantioselectivity in these catalytic reactions, we examined some stoichiometric reactions of planar-chiral Cp′Ru complexes with allylic compounds. We report here the reaction of planar-chiral Cp′Ru complexes with allyl chlorides to give π-allyl complexes with metal-centered chirality and high diastereoselectivity.

We started our investigation with the reaction of planar-chiral Cp′Ru complexes (**1**) with 1,3-diphenylallyl ethyl carbonate. However, no reaction took place and the starting materials were recovered. In the reaction with 1,3-diphenyl-2-propenyl chloride, the starting materials were consumed, but we could not confirm the structure of the products. We next examined the reaction using allyl chloride with no substituents.

Treatment of the Cp′Ru complex **1a** with 10 equiv of allyl chloride in acetone at room temperature led to the formation of a π-allyl complex (**2a**) in 83% yield (eq 1).[5,6]



Since complex **2a** has a three-legged piano-stool structure with different ligands, metal-centered chirality is generated at the Ru atom.[7] Thus, complex **2a** consisted of two diastereomers, and the ^{31}P NMR spectrum suggested that the ratio was 89% de. The highly diastereoselective oxidative addition to planar-chiral Cp′ complexes of Rh and Ir has also been reported by other groups.[8] In the differential NOE spectra of the major product, irradiation of the methyl signal at the 4-position on the Cp′ ring gave rise to NOE signals of the allyl protons at the anti position, whereas the NOE signal that was assignable to one of the two syn allylic protons was observed upon irradiation of the methyl signal at the 2-position of the Cp′ group.[9] These results clearly

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Table 1. Reaction of Ruthenium Complexes 1 with Allyl and Methallyl Chlorides

entry	complex	substrate	product	yield/%[a]	de/%[a,b]
1	**1a**	allyl chloride	**2a**	83	89 (I)
2	**1b**	allyl chloride	**2b**	75	94 (I)
3	**1c**	allyl chloride	**2c**	81	80 (II)
4	**1a**	methallyl chloride	**3a**	83	96 (I)
5	**1b**	methallyl chloride	**3b**	74	98 (I)
6	**1c**	methallyl chloride	**3c**	53	60 (II)

[a] Determined by ^{31}P NMR. [b] The structure of the major product is given in parentheses; see eq 1.

suggested that the π-allyl group coordinates to the Ru atom in an endo fashion with a configuration of $S_{Cp}S_{Ru}/R_{Cp}R_{Ru}$ (**I**).

Reactions of complexes **1b**,**c**, which have phenyl and *tert*-butyl groups at the 4-position on the Cp′ ring instead of a methyl group as in **1a**, also gave π-allyl complexes **2b**,**c** with high diastereoselectivity, respectively (Table 1). Whereas the configuration of the major isomer of complex **2b** was $S_{Cp}S_{Ru}/R_{Cp}R_{Ru}$ (**I**), the major isomer of complex **1c** had a configuration of $S_{Cp}R_{Ru}/R_{Cp}S_{Ru}$ (**II**). Reactions of complexes **1a**−**c** with methallyl chloride gave the π-methallyl complexes **3a**−**c**, respectively. The configuration at the Ru atom in the major isomer of complex **3c** was opposite to those of complexes **3a**,**b**. Similar phenomena were observed in ligand exchange reactions of planar-chiral Cp′Ru complexes with an iodide ligand.[9b] The molecular structure of the major isomer of π-methallyl complex **3a-I** was unequivocally established by X-ray analysis (Figure 1).[10] As predicted from the NOE spectrum, the orientation of the π-methallyl group was endo and the configuration was $S_{Cp}S_{Ru}/R_{Cp}R_{Ru}$. In the catalytic allylic substitution, the absolute configuration of the products varied according to the substituent at the 4-position on the Cp′ ring of complex **1**. Since the π-allyl complex is known to be an intermediate in catalytic allylic substitutions,[5,11] the present results strongly suggest that the stereochemistry in the catalytic reactions must depend on the chirality at the Ru center in π-allyl complexes.

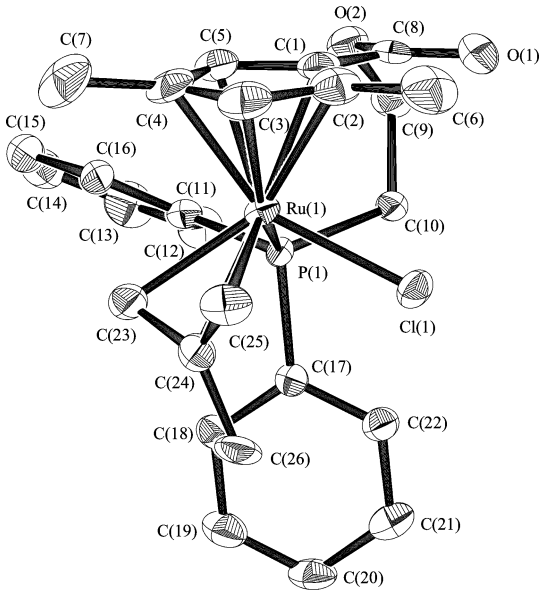
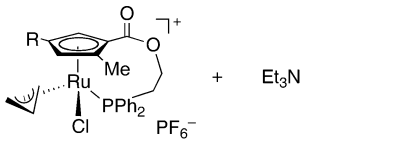


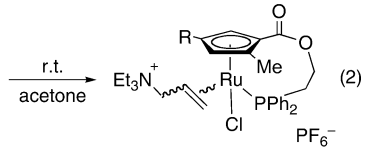
Figure 1. Molecular structure of complex **3a-I**. Hydrogen atoms and PF_6^- counteranion are omitted for clarity.

In complexes **2** and **3**, epimerization between **I** and **II** did not take place at room temperature but did occur at higher temperature. Heating a nitromethane solution of complex **2c** (**I**/**II** = 10/90) at 90 °C for 6 h changed the **I**/**II** ratio to 66/34. Although the solution of complex **2c** (**I**/**II** = 66/34) was left to stand at room temperature for a long time, the ratio of the isomers did not change at all. These results suggest that the diastereoselectivity in the oxidative addition of allyl chlorides is under kinetic control, as was also supported by the experimental finding that the diastereoselectivity of complex **2c** decreased to 42% de in the reaction of complex **1c** with allyl chloride at 40 °C.

Next, we examined the reactivity of π-allyl complexes with amine. The reaction of complex **2a-I**, which was isolated as a diastereomerically pure sample from a mixture with **2a-II**, with 1.1 equiv of triethylamine in acetone at room temperature resulted in the formation of an olefin complex (**4a**) in 82% yield (eq 2), while the



2a-I: R = Me
2b-I: R = Ph



(2)

4a: R = Me
4b: R = Ph

(6) The preparation of **2a** is as follows: to a solution of complex **1a** (136 mg, 0.2 mmol) in acetone (2 mL) was added allyl chloride (160 μL, 2.0 mmol), and the mixture was stirred for 36 h at room temperature. After the addition of diethyl ether, the resulting orange precipitate was collected and washed several times with diethyl ether to give complex **2a** (112 mg, 83%). IR (cm^{-1}, KBr): 1741 ($\nu_{C=O}$). FAB MS: m/z 527 (M − PF_6^-). Anal. Calcd for $C_{25}H_{27}ClF_6O_2P_2Ru$: C, 44.69; H, 4.05; Cl, 5.28. Found: C, 44.79; H, 4.31; Cl, 5.20. Data for the major product **2a-I** are as follows. ^{1}H NMR (acetone-d_6, 600 MHz): δ 7.82−7.45 (m, 10H, Ph), 6.48 (s, 1H, Cp′ H^5), 6.29 (s, 1H, Cp′ H^3), 5.06 (ddd, 1H, J = 7.7, 11.3, 24.2 Hz, OCH_2), 4.72 (dd, 1H, J = 2.5, 11.3 Hz, allyl H^4), 4.54−4.51 (m, 1H, allyl H^1), 4.10−4.09 (m, 1H, allyl H^2), 3.96−3.91 (m, 1H, OCH_2), 3.56−3.50 (m, 1H, CH_2P), 3.31−3.26 (m, 1H, allyl H^3), 2.75 (d, 1H, J = 10.7 Hz, allyl H^5), 2.23 (d, 3H, J = 1.4 Hz, Cp′ Me^2), 1.96 (s, 3H, Cp′ Me^4). ^{13}C NMR (CD_3NO_2, 150 MHz): δ 165.4 (C=O), 135.8−126.8 (Ph), 125.2 (Cp′ C^1), 108.1 (Cp′ C^4), 104.1 (Cp′ C^3), 99.5 (allyl C^2), 93.7 (Cp′ C^2), 89.9 (Cp′ C^5), 70.6 (allyl C^1), 65.4 (allyl C^3), 62.2 (d, J = 5 Hz, CH_2O), 21.4 (d, J = 40 Hz, CH_2P), 13.1 (Cp′ Me^2), 12.9 (Cp′ Me^4). ^{31}P NMR (acetone-d_6, 160 MHz): δ 34.1. Data for the minor product **2a-II** are as follows. ^{31}P NMR (acetone-d_6, 160 MHz): δ 25.3. See the Supporting Information for the assignment of the signals due to the allyl groups in ^{1}H and ^{13}C NMR.

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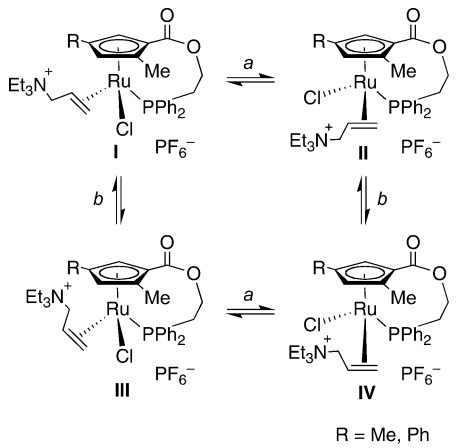
(10) Crystallographic data for **3a-I**: formula $C_{26}H_{29}ClF_6O_2P_2Ru$, fw = 685.97, monoclinic, space group $P2_1/c$ (No. 14), a = 10.992(5) Å, b = 17.793(6) Å, c = 14.320(4) Å, β = 101.13(3)°, V = 2747(1) Å^3, Z = 4, d_{calcd} = 1.658 g cm^{-3}, −75 °C, ω−2θ scan, 6° < 2θ < 55°, μ(Mo Kα) = 8.48 cm^{-1}, R (R_w) = 0.065 (0.089) for 343 parameters against 4620 reflections with $I > 3.0\sigma(I)$ out of 6310 unique reflections (R_{int} = 0.178) by the full-matrix least-squares method, GOF = 1.12.

Scheme 1. Possible Structure of Complex 4[a]



[a] Legend: (a) epimerization at the Ru center; (b) face flip of the olefin ligand.

Table 2. Reaction of Ruthenium Complexes 2-I with Triethylamine

entry	complex	temp/°C	product	yield/%[a]	de/%[a]
1	**2a-I**	20	**4a**	82	38
2	**2a-I**	0	**4a**	94	71
3	**2a-I**	−40	**4a**	>99	>99
4	**2a-I**	−78	**4a**	>99	>99
5	**2b-I**	20	**4b**	96	42
6	**2b-I**	0	**4b**	98	51
7	**2b-I**	−40	**4b**	97	92
8	**2b-I**	−78	**4b**	>99	>99

[a] Determined by ^{31}P NMR.

reaction with dipropylamine gave a complex mixture. Although we could not isolate complex **4a** from the reaction mixture, the structure was confirmed on the basis of comparison of the ^{1}H NMR spectrum to that of an analogous Ru complex.[5d] The ^{31}P NMR spectrum of complex **4a** suggested that the diastereoselectivity was 38% de. A similar reaction of diastereomerically pure **2b-I** gave an olefin complex (**4b**) in 96% yield with 42% de. When the reaction was performed at lower temperature, the yield and diastereoselectivity were increased (Table 2). For example, the reaction of complex **2a-I** at −40 °C produced a single diastereomer of complex **4a**. However, when the solution of the single diastereomer of **4a** was warmed at room temperature, a mixture of two diastereomers in 38% de, which is the same selectivity as in the reaction at room temperature, was obtained, suggesting that the olefin complex **4** was in an equilibrium state at room temperature. As shown in Scheme 1, there are four possible structures for complex **4**. Each of them can be generated by the epimerization at the Ru center (a) and the face flip of the olefin ligand (b). Although we tried to determine the stereochemistry of complex **4** by spectral analyses such as NOE experiments and 2D NMR, no useful information was obtained. However, the facile face flip of the olefin ligand was known in chiral CpRe complexes, in which the configuration at the chiral metal center did not change.[12] Thus, complex **4** likely consists of **4-I** and/or **4-III**.

In summary, we have described the diastereoselective formation of π-allyl−Ru complexes by the oxidative addition of allyl chloride to planar-chiral Cp′Ru complexes under kinetic control. These results should provide useful information for understanding the mechanism of asymmetric allylic substitution catalyzed by planar-chiral Cp′Ru complexes. Further studies are now in progress.

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Supporting Information Available: Text giving experimental details and full characterization data for complexes **2** and **3**, and a CIF file giving crystallographic data for complex **3a-I**. This material is available free of charge via the Internet at http://pubs.acs.org.

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