Synthesis, Structures, and Reactivities of Rhodium and Ruthenium Complexes with a Novel Chiral Cyclopentadienyl−Ferrocenyldiphenylphosphine Bidentate Ligand

Yoshiaki Nishibayashi, Izuru Takei, and Masanobu Hidai*

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, Hongo, Tokyo 113, Japan

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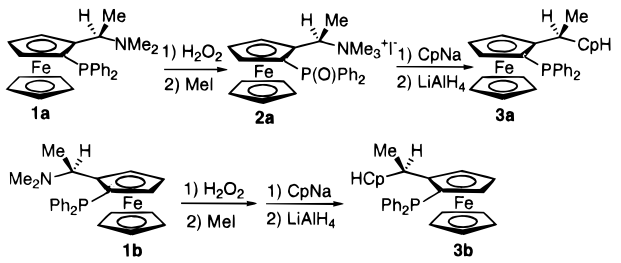
Summary: Novel rhodium(I) and ruthenium(II) complexes with the chiral cyclopentadienyl−phosphine bidentate ligand PPFCp have been prepared and characterized crystallographically. The cationic ruthenium−vinylidene complex [Ru(C=CHPh)(PPh$_3$)(PPFCp)]PF$_6$, obtained from [RuCl(PPh$_3$)(PPFCp)] and phenylacetylene, reacts with 1-buten-3-ol to afford 3-methyl-1-phenyl-4-penten-2-one in moderate yield with moderate enantioselectivity.

The molecular design of an appropriate chiral ligand is essential in transition-metal-catalyzed asymmetric reactions to obtain highly enantiomerically pure compounds. Consequently, many studies have currently focused on the preparation of new efficient ligands.[1] A variety of early-transition-metal-catalyzed asymmetric reactions using chiral cyclopentadienyl ligands have been reported during the last few years.[2] In particular, the chiral C_2-symmetric *ansa*-metallocenes of titanium and zirconium have found notable application as catalysts for enantioselective catalytic reactions.[2] However, the ruthenium-catalyzed asymmetric reactions using chiral cyclopentadienyl ligands are limited, in spite of the development of unique catalytic activities of the η^5-cyclopentadienyl (Cp) or η^5-pentamethylcyclopentadienyl (Cp*) ruthenium complexes.[3,4] In the Cp-containing ruthenium complexes, the cyclopentadienyl moiety is free to rotate about the cyclopentadienyl-ruthenium axis, so that a suitable chiral enviroment is not effectively made around the metal.[5] Here we envisage the preparation of a new type of a chiral cyclopentadienyl−phosphine bidentate ligand to prevent the rotation of the Cp ring. The preliminary results of the preparation of rhodium and ruthenium complexes containing the new chiral ligand and their application to asymmetric synthesis are described below.

Scheme 1



Our investigations of the synthesis of optically active cyclopentadienyl−phosphine bidentate ligands started with the utilization of chiral ferrocenes with planar chirality because the latter ligands are of increasing importance in stoichiometric and catalytic asymmetric synthesis using transition-metal complexes.[6,7] The optically active chiral ligand (*S*,*S*)-PPFCpH (**3a**) was prepared from the corresponding quaternary ammonium salt **2a** by the introduction of a cyclopentadienyl moiety into the pseudo benzylic position of ferrocene and the following reduction of the phosphine oxide by $LiAlH_4$ (Scheme 1). The nucleophilic substitution reaction proceeded with the complete retention of configuration at the stereogenic center.[8] Thus, the chiral ligand **3a** was synthesized by four steps in 46% overall yield. Similarly, (*R*,*R*)-PPFCpH (**3b**) was obtained from (*S*,*R*)-PPFA (**1b**) (Scheme 1).

The reaction of (*R*,*R*)-PPFCpH (**3b**), after being treated with an equimolar amount of *sec*-BuLi, with

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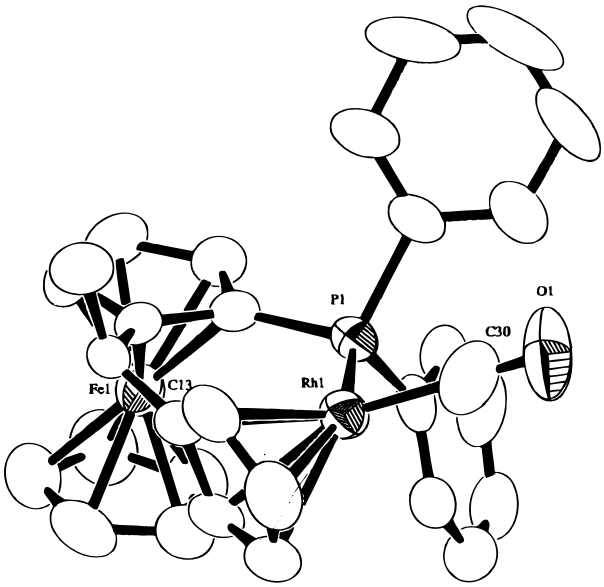
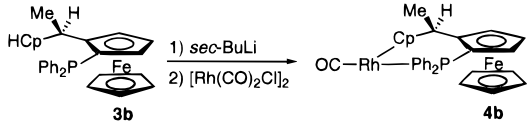
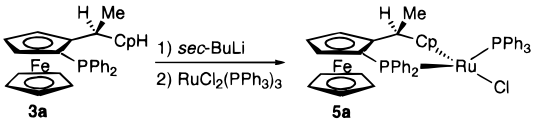


Figure 1. Molecular structure of **4b**. Selected bond distances (Å) and angles (deg): Rh(1)−P(1) = 2.214(2), Rh(1)−C(13) = 2.234(8), Rh(1)−C(30) = 1.819(9); P(1)−Rh(1)−C(13) = 96.6(2), P(1)−Rh(1)−C(30) = 93.2(3), C(13)−Rh(1)−C(30) = 157.9(3).

Scheme 2



Scheme 3



$[Rh(CO)_2Cl]_2$ in a 2:1 molar ratio in THF at room temperature for 12 h afforded the mononuclear rhodium(I) complex Rh(CO)[(*S*,*R*)-PPFCp] (**4b**) in 66% isolated yield (Scheme 2). The structure of **4b** was determined by ^{1}H and ^{31}P NMR.[9] The cyclopentadienyl−phosphine chelation structure of **4b** was unequivocally confirmed by X-ray analysis.[10] An ORTEP drawing of one of the two independent molecules of **4b** in each unit cell is shown in Figure 1 along with selected bond distances and angles. The rhodium atom has a distorted-trigonal-planar geometry.

The reaction of the lithium salt of **3a** with $[RuCl_2(PPh_3)_3]$ produced the ruthenium(II) complex [RuCl(PPh$_3$)[(*R*)-(*S*)-PPFCp]] (**5a**) as orange crystals after recrystallization from EtOH in 75% yield (Scheme 3). Both ^{1}H and ^{31}P NMR revealed that the complex **5a** was a pure diastereoisomer.[11] In order to determine the absolute configuration around the ruthenium atom, the single-crystal X-ray diffraction analysis of **5a** was carried out.[12] An ORTEP drawing of the molecular structure of **5a** is shown in Figure 2 along with selected bond distances and angles. The stereogenic ruthenium center has an *S* configuration, provided that the priority sequence is in the order η^5-Cp > Cl > P(ferrocene)Ph$_2$ > PPh$_3$.[13] Rhodium and ruthenium complexes with Cp−P bidentate chiral ligands derived from L-threitol or (*S*,*S*)-1,2-*trans*-bis(hydroxymethyl)cyclopentane have already been reported; however, the detailed structures were not determined.[14]

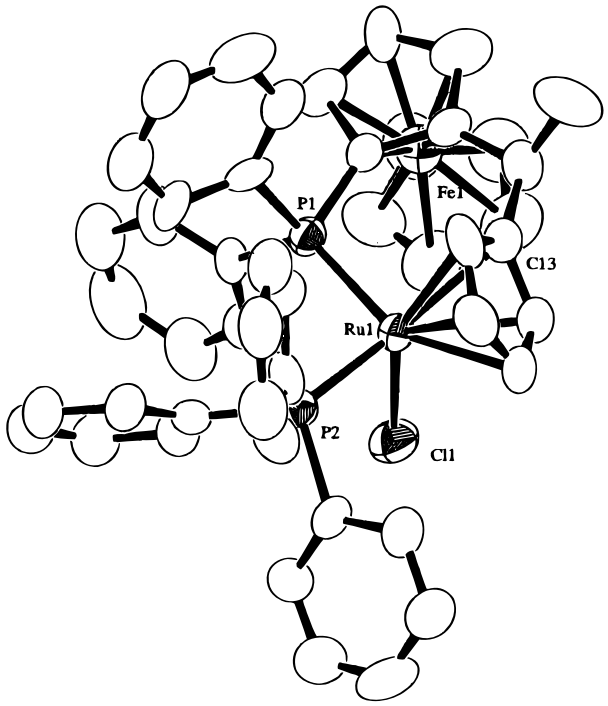


Figure 2. Molecular structure of **5a**. Selected bond distances (Å) and angles (deg): Ru(1)−Cl(1) = 2.459(3), Ru(1)−P(1) = 2.332(3), Ru(1)−P(2) = 2.309(4), Ru(1)−C(13) = 2.26(1); Cl(1)−Ru(1)−P(1) = 99.3(1), Cl(1)−Ru(1)−P(2) = 88.7(2), Cl(1)−R(1)−C(13) = 117.7(4), P(1)−Ru(1)−P(2) = 99.6(1), P(1)−Ru(1)−C(13) = 90.5(4), P(2)−Ru(1)−C(13) = 150.0(4).

When the ruthenium complex **5a** was treated with phenylacetylene at room temperature in the presence of NH_4PF_6, the ruthenium vinylidene complex [Ru(C=CHPh)(PPh$_3$)[(*R*)-(*S*)-PPFCp]]PF$_6$ (**6a**) was obtained as orange crystals from acetone-diethyl ether in 96% yield (Scheme 4). ^{1}H and ^{31}P NMR revealed that complex **6a** was a pure diastereomer.[15] The X-ray

(9) Spectroscopic and analytical data for **4b**: ^{1}H NMR δ 1.19 (d, 3H, J = 7.0 Hz), 3.65 (m, 1H), 3.93 (s, 5H), 3.95 (m, 1H), 4.18 (m, 1H), 4.42 (m, 1H), 5.27 (m, 1H), 5.46 (m, 1H), 5.61 (m, 1H), 5.76 (m, 1H), 7.2−7.9 (m, 10H); ^{31}P NMR δ 45.7 (d, J = 197 Hz). Anal. Calcd for $C_{30}H_{26}$FeOPRh: C, 60.84; H, 4.43. Found: C, 60.59; H, 4.08.

(10) Crystallographic data for **4b**: $C_{30}H_{26}$FeOPRh, orthorhombic, space group $P2_12_12_1$ (No.19), a = 15.614(6) Å, b = 33.912(9) Å, c = 9.544(7) Å, V = 5053(4) Å^3, Z = 8, D_{calcd} = 1.557 g cm^{-3}, μ(Mo Kα) = 13.09 cm^{-1}, R = 0.040, R_w = 0.023 for 4109 unique reflections ($I > 3\sigma(I)$).

(11) Spectroscopic and analytical data for **5a**: ^{1}H NMR δ 1.33 (d, 3H, J = 7.0 Hz), 3.04 (m, 1H), 3.51 (m, 1H), 3.94 (m, 1H), 4.12 (s, 5H), 4.29 (m, 1H), 4.30 (m, 1H), 4.48 (m, 1H), 4.57 (m, 1H), 5.20 (m, 1H), 6.44 (m, 2H), 6.87 (m, 2H), 7.0−8.1 (m, 21H); ^{31}P NMR δ 28.5 (d, J = 41 Hz), 45.5 (d, J = 41 Hz). Anal. Calcd for $C_{47}H_{41}ClFeP_2Ru\cdot 2EtOH$: C, 64.34; H, 5.61. Found: C, 64.10; H, 5.28.

(12) Crystallographic data for **5a**: $C_{47}H_{41}ClFeP_2Ru\cdot 2EtOH$, monoclinic, space group $P2_1$(No. 4), a = 10.992(2) Å, b = 13.099(2) Å, c = 15.595(2) Å, β = 93.43(2)°, V = 2241.4(6) Å^3, Z = 2, D_{calcd} = 1.411 g cm^{-3}, μ(Mo Kα) = 8.31 cm^{-1}, R = 0.074, R_w = 0.084 for 3960 unique reflections ($I > 3\sigma(I)$).

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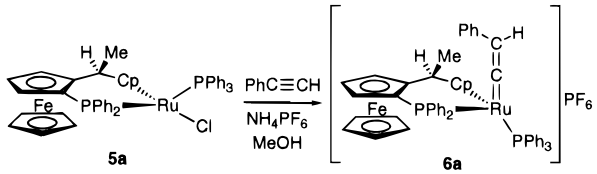
(15) Spectroscopic and analytical data for **6a**: ^{1}H NMR δ 1.45 (d, 3H, J = 7.0 Hz), 3.07 (m, 1H), 3.97 (s, 5H), 4.19 (m, 1H), 4.30 (m, 1H), 4.67 (m, 1H), 4.86 (m, 1H), 5.13 (m, 1H), 5.27 (m, 1H), 5.35 (m, 1H), 5.74 (m, 1H), 6.89 (m, 2H), 6.8−7.4 (m, 28H); ^{31}P NMR δ 31.8 (d, J = 27 Hz) and 44.9 (d, J = 27 Hz). Anal. Calcd for $C_{55}H_{48}F_6FeP_3Ru$: C, 61.58; H, 4.51. Found: C, 61.19; H, 4.89.

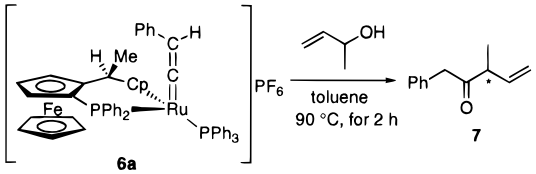
Scheme 4



diffraction analysis of **6a** was performed to determine the absolute configuration around the ruthenium atom.[16] It confirms that this reaction proceeds with inversion of configuration at the ruthenium center. This is in sharp contrast to the reaction of cyclopentadienyl ruthenium complexes containing chiral diphosphine ligands with terminal alkynes such as CHIRAPHOS and PROPHOS, where the reaction is completely stereospecific with retention of configuration at the ruthenium center.[17]

Recently, Trost et al. reported the reconstitutive condensation of both allylic alcohols and terminal alkynes by using $[CpRuCl(PPh_3)_2]$, where the reaction was considered to proceed via a ruthenium vinylidene.[18] This reconstitutive condensation did not proceed when cyclopentadienylruthenium complexes with chelate diphosphines were used.[18,19] In this context, we employed complex **6a** as a catalyst for this asymmetric condensation. Treatment of the ruthenium vinylidene complex **6a** with excess amounts of 1-buten-3-ol at 90 °C for 2 h in toluene resulted in the formation of 3-methyl-1-phenyl-4-penten-2-one (**7**) in 40% yield with 65% enantiomeric excess (ee) (Scheme 5).[20] This provides the first example of an asymmetric reaction via a chiral vinylidene complex as the chiral source. Furthermore, the asymmetric reconstitutive condensation between phenylacetylene and 1-buten-3-ol was performed in the presence of 10 mol % of **5a** and 20 mol % of NH_4PF_6 at 90 °C for 2 h in toluene. The chemical yield of **7** was 10% with an ee value of 25%.[20] The difference in enantioselectivity between the stoichiometric and catalytic reactions suggests that the reaction of **5a** with phenylacetylene does not proceed stereospecifically at 90 °C. Actually, it was observed that treatment of **5a** with an excess amount of phenylacetylene in the presence of NH_4PF_6 at 90 °C immediately afforded a mixture of ruthenium vinylidene diastereomers (the ratio of diastereomers observed by ^1H NMR spectroscopy was ca. 70:20:10). Furthermore, treatment of these ruthenium vinylidene diastereomers with excess amounts of 1-buten-3-ol at 90 °C for 2 h in toluene resulted in the formation of **7** in 55% yield with 21% ee. In order to achieve a higher selectivity in this catalytic reaction, this problem has to be solved. Further studies of the catalytic reaction[21] using **5** or **6** and the determination of the absolute configuration of **7** are now in progress.

Scheme 5



Supporting Information Available: Text, tables, and figures giving details of the X-ray structure study of complexes **4b**, **5a**, and **6a** (74 pages). Ordering information is given on any current masthead page.

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(16) Preliminary crystallographic data for **6a**: $C_{55}H_{48}F_6FeP_3Ru \cdot Et_2O$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 18.794(8)$ Å, $b = 21.164(5)$ Å, $c = 13.759(6)$ Å, $V = 5472(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.392$ g cm^{-3}, μ(Mo Kα) = 6.88 cm^{-1}, $R = 0.078$, $Rw = 0.085$ for 1944 unique reflections ($I > 3\sigma(I)$). The carbon atoms of cyclopentadienyl rings and ruthenium, iron, and phosphine atoms were refined anisotropically. All other non-hydrogen atoms were refined isotropically.

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(20) The low yield of **7** for both the stoichiometric and catalytic reactions was due to the formation of unidentified side products.

(21) The preliminary results of a few catalytic reactions using **5** are as follows: 1-octyne and 1-buten-3-ol (20%, 34% ee), 1-octyne and 4-methyl-1-penten-3-ol (10%, 27% ee). The results will be reported in due course.