

Synthesis of ruthenium complexes with planar-chiral cyclopentadienyl-pyridine or -phosphine bidentate ligands

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Novel ruthenium complexes possessing planar-chiral cyclopentadienyl-pyridine or -phosphine bidentate ligands have been synthesized from (trisubstituted cyclopentadienyl)(benzene)ruthenium complexes. Co-ordination of the pyridyl group linked to a cyclopentadienyl ring through an ester bond is fairly weak, so that the pyridine dissociates from the central ruthenium atom in acetonitrile. In contrast, the phosphine ligand tightly co-ordinates to the ruthenium even in acetonitrile. Enantiomerically pure samples of planar-chiral cyclopentadienylphosphine complexes have been prepared by use of optically pure ruthenium complexes as a starting material. The molecular structure of a neutral ruthenium dithiocarbamate complex with the cyclopentadienylphosphine bidentate ligand has been determined by X-ray crystallography.

Introduction

It is widely accepted that optically active organometallic complexes are powerful tools for asymmetric organic syntheses as effective catalytic or stoichiometric mediators.¹ Half-sandwich complexes MCpL_3 , which are referred to as “three-legged piano stools”, have a rich chemistry and chiral versions have been applied to asymmetric catalysis.² There are several examples of asymmetric reactions catalysed by half-sandwich complexes with chiral ligands.³ Although some optically active complexes with a chiral metal center have also been prepared, application of these complexes is limited to stoichiometric reactions since racemization at the chiral metal center often takes place during the reactions.⁴ Planar-chiral cyclopentadienyl metal complexes should be useful as asymmetric catalysts because racemization arising from a change in co-ordination mode from η^5 into η^1 or dissociation of the cyclopentadienyl group is unlikely to occur. The efficiency of planar-chiral cyclopentadienyl complexes has proved particularly valuable in the polymerization of olefins by bis(cyclopentadienyl) complexes (metallocenes) of Group IV metals.⁵ On the other hand, few studies on planar-chiral cyclopentadienyl complexes of late transition metals have so far been made though they have great potential as catalysts in novel asymmetric reactions.⁶ Recently Fu and co-workers⁷ described asymmetric reactions using planar-chiral ferrocene derivatives as catalysts,⁷ in which, however, metal atoms with planar-chiral ligands do not act as a reactive site.

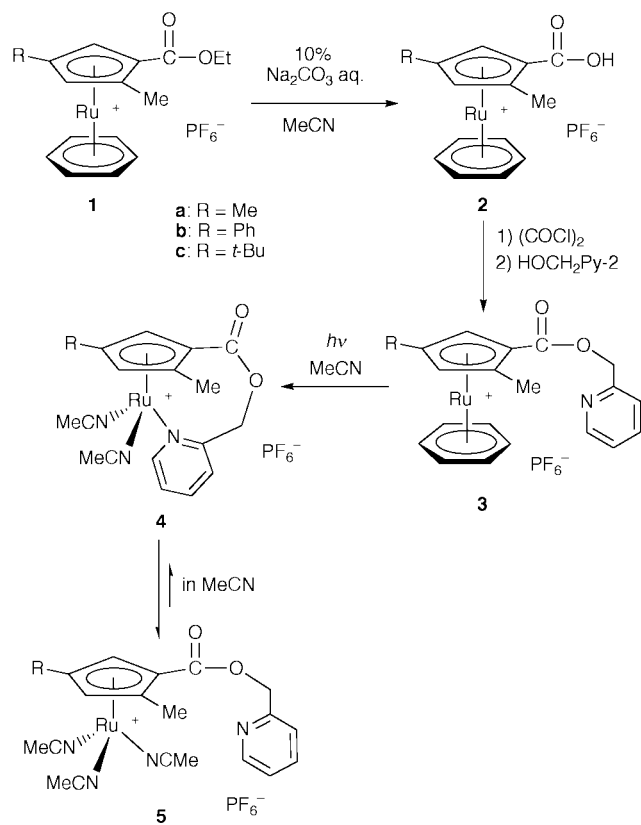
Previously we have reported the syntheses of planar-chiral organometallic complexes of late transition metals with trisubstituted η^5 -cyclopentadienyl ligands.^{8,9} As a fundamental investigation of the application of planar-chiral complexes to asymmetric catalysis, we have examined some stoichiometric reactions of these planar-chiral complexes. The stereoselectivities induced by these planar chiral complexes, however, are not high. One possible reason may be rotation of the cyclopentadienyl groups, which could cause corruption of the asymmetric environment around a reactive metal center. In order to prevent this we set out to tether the cyclopentadienyl group to anchor ligands.¹⁰ Herein we report the synthesis of enantiomerically pure planar-chiral cyclopentadienyl ruthenium complexes possessing such anchor ligands. Although a few planar-chiral complexes with cyclopentadienyl- and indenyl-phosphine

bidentate ligands have been prepared as racemic mixtures,⁶ this is the first example of an enantiomerically pure one. Very recently planar-chiral η^6 -arene complexes with anchor ligands have been isolated in an optically pure state by Ward and co-workers.¹¹

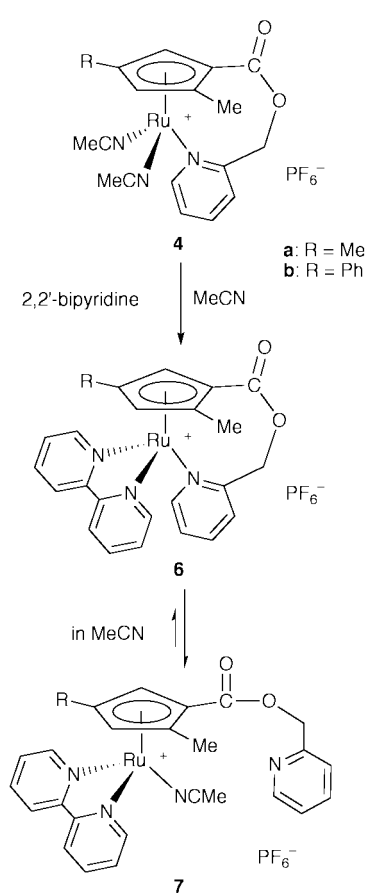
Results and discussion

First we chose pyridine as an anchor ligand and attempted to synthesize cyclopentadienylpyridine ruthenium complexes. Cationic ruthenium complexes $[\text{Ru}\{\eta^5\text{-C}_5\text{H}_2(\text{Me})(\text{R})\text{CO}_2\text{Et}\}(\eta^6\text{-C}_6\text{H}_6)][\text{PF}_6]$ (R = Me **1a**, Ph **1b** or *t*-Bu **1c**) that possess a trisubstituted cyclopentadienyl ligand with an exchangeable ester group were used as starting materials.⁹ Hydrolysis of **1a–1c** under basic conditions gave carboxylic acid analogs $[\text{Ru}\{\eta^5\text{-C}_5\text{H}_2(\text{Me})(\text{R})\text{CO}_2\text{H}\}(\eta^6\text{-C}_6\text{H}_6)][\text{PF}_6]$ (R = Me **2a**, Ph **2b** or *t*-Bu **2c**) (Scheme 1). A 2-pyridyl group was introduced by esterification with 2-NC₅H₄CH₂OH using a standard method to give $[\text{Ru}\{\eta^5\text{-C}_5\text{H}_2(\text{Me})(\text{R})\text{CO}_2\text{CH}_2\text{C}_5\text{H}_4\text{N}\}(\eta^6\text{-C}_6\text{H}_6)][\text{PF}_6]$ (R = Me **3a** or Ph **3b**). Irradiation with UV light in CH₃CN caused dissociation of the η^6 -benzene ligand to give $[\text{Ru}\{\eta^5, \eta^1\text{-C}_5\text{H}_2(\text{Me})(\text{R})\text{CO}_2\text{CH}_2\text{C}_5\text{H}_4\text{N}\}(\text{CH}_3\text{CN})_2][\text{PF}_6]$ (R = Me **4a** or Ph **4b**) in quantitative yields.¹² The elemental analysis showed that the proposed structure is consistent with the composition of **4a**. However, complexes **4a** and **4b** are unstable in common organic solvents other than acetonitrile even at low temperature. In their ¹H NMR spectra in acetonitrile-*d*₃, chemical shifts of the signals attributed to pyridyl protons were very similar to those of **3a** and **3b**, respectively. These data suggest that the pyridyl groups of **4a** and **4b** dissociate from the ruthenium atom to generate $[\text{Ru}\{\eta^5\text{-C}_5\text{H}_2(\text{Me})(\text{R})\text{CO}_2\text{CH}_2\text{C}_5\text{H}_4\text{N}\}(\text{CH}_3\text{CN})_3][\text{PF}_6]$ (R = Me **5a** or Ph **5b**) in acetonitrile.

On treatment of complexes **4a** and **4b** with bipyridine in acetonitrile, two acetonitrile ligands were replaced by 2,2'-bipyridine to give $[\text{Ru}\{\eta^5, \eta^1\text{-C}_5\text{H}_2(\text{Me})(\text{R})\text{CO}_2\text{CH}_2\text{C}_5\text{H}_4\text{N}\}(\text{bipy})][\text{PF}_6]$ (R = Me **6a** or Ph **6b**) (Scheme 2) which are stable not only in acetonitrile but also in acetone at room temperature. The ¹H NMR spectra of **6a**, which were measured both in acetonitrile-*d*₃ and in acetone-*d*₆, are shown in Fig. 1 along with that of **3a** in acetone-*d*₆. The signals assigned to α - and γ -protons of the anchor pyridyl group in **3a** were observed at δ 8.66 and 7.87, respectively. There is no significant difference in



Scheme 1



Scheme 2

these chemical shifts between acetonitrile- d_3 and acetone- d_6 . The ^1H NMR spectrum of **6a** in acetonitrile- d_3 showed signals due to the pyridyl protons of the anchor ligand at δ 8.54 and 7.72, which are close to those of **3a**. In contrast, the signals

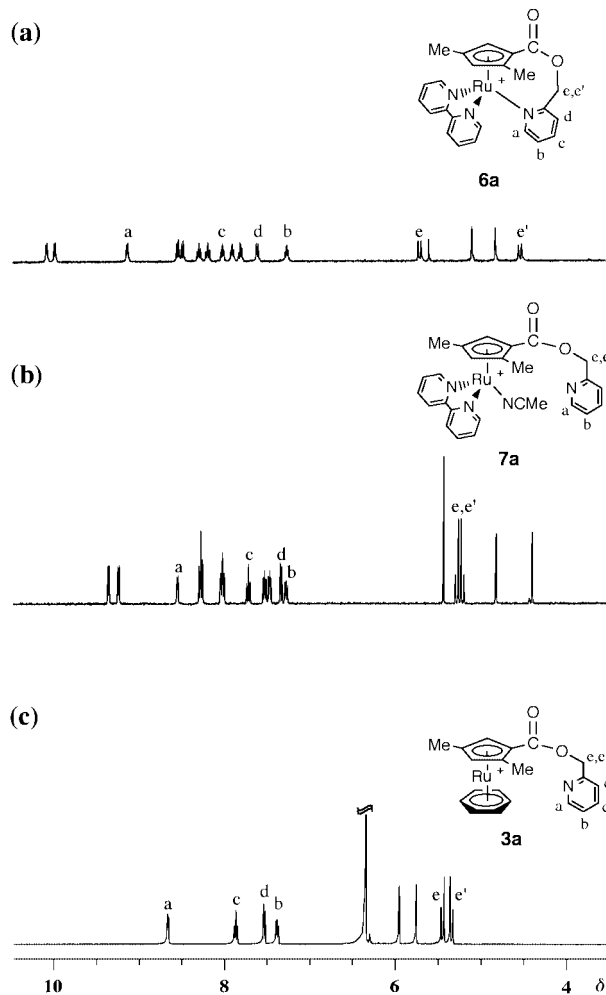
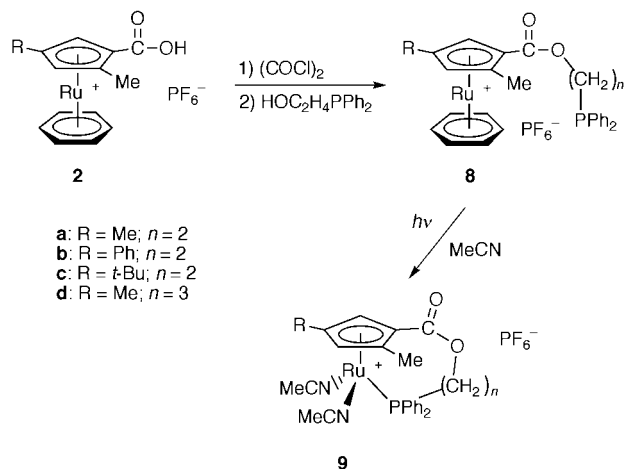


Fig. 1 The ^1H NMR spectra of cyclopentadienylpyridine ruthenium complexes: (a) **6a** in acetone- d_6 , (b) **6a** in acetonitrile- d_3 generating **7a** and (c) **3a** in acetone- d_6 .

attributed to the pyridyl protons at α - and γ -positions of **6a** were observed at δ 9.14 and 8.02 in acetone- d_6 , respectively. These data indicate that the pyridyl group of **6a** dissociates from the ruthenium atom in acetonitrile to form an acetonitrile complex, $[\text{Ru}\{\eta^5\text{-C}_5\text{H}_2(\text{Me})(\text{R})\text{CO}_2\text{CH}_2\text{C}_5\text{H}_4\text{N}\}(\text{bipy})(\text{CH}_3\text{CN})][\text{PF}_6^-]$ (R = Me **7a** or Ph **7b**), but co-ordinates in acetone. The signals of methylene protons on the tether were observed as two diastereotopic doublets due to the planar chirality of the cyclopentadienyl group. It may be of interest that the difference in the chemical shift between the two diastereotopic methylene protons of **6a** in acetone is much larger than that in acetonitrile. Two methylene signals were observed at δ 5.72 and 4.55 in acetone- d_6 whereas δ equals 5.28 and 5.21 in acetonitrile- d_3 , respectively. The co-ordination of the pyridyl group would amplify the magnetic inequivalency of the geminal protons.¹³

Since co-ordination of the anchor pyridyl group seems to be weak, it was changed to a diphenylphosphino group, which was similarly introduced by esterification of complexes **2a–2c** with $\text{HO}(\text{CH}_2)_n\text{PPh}_2$.¹⁴ However, the co-ordination of η^6 -benzene is so strong that the phosphorus atom does not co-ordinate to the ruthenium atom in $[\text{Ru}\{\eta^5\text{-C}_5\text{H}_2(\text{Me})(\text{R})\text{CO}_2(\text{CH}_2)_n\text{PPh}_2\}(\eta^6\text{-C}_6\text{H}_6)][\text{PF}_6^-]$ (R = Me, $n = 2$ **8a**; R = Ph, $n = 2$ **8b**; R = *t*-Bu, $n = 2$ **8c**; R = Me, $n = 3$ **8d**) (Scheme 3). Irradiation by UV light in CH_3CN caused dissociation of the η^6 -benzene ligand to give $[\text{Ru}\{\eta^5, \eta^1\text{-C}_5\text{H}_2(\text{Me})(\text{R})\text{CO}_2(\text{CH}_2)_n\text{PPh}_2\}(\text{CH}_3\text{CN})_2][\text{PF}_6^-]$ (R = Me, $n = 2$ **9a**; R = Ph, $n = 2$ **9b**; R = *t*-Bu, $n = 2$ **9c**; R = Me, $n = 3$ **9d**) in quantitative yields.¹² Complexes **9a–9d** are stable in air and soluble in polar solvents such as dichloromethane, chloroform and acetone.



Scheme 3

Complexes **9a–9d** were fully characterized by means of spectral analyses. The FAB mass spectrum of **9a** revealed a peak at $m/z = 533$, which corresponds to the cationic species containing Ru, suggesting that **9a** has two CH_3CN ligands as well as a cyclopentadienylphosphine ligand in the molecule. The result of elemental analysis also supported the composition of **9a**. The ^{31}P NMR of **9a** showed a singlet at δ 35.56, while the signal of complex **8a** was observed at much higher magnetic field (δ –20.89). The remarkable difference in chemical shifts of the ^{31}P NMR spectra between **9a** and **8a** indicates the co-ordination of an anchor PPh_2 group linked by the tether to a cyclopentadienyl ligand.¹⁵ The ^1H NMR spectrum of **9a** in CDCl_3 exhibited four multiplet signals assignable to the protons of two methylene groups on the tether as observed for **6a** in acetone- d_6 . The signals attributable to the protons of two CH_3CN ligands appeared as two doublets due to coupling with the phosphorus nucleus. Similarly in the ^{13}C NMR spectrum of **9a**, coupling with the phosphorus atom was also found for the signals due to cyclopentadienyl carbon at the 3 position. These data clearly identified the structure of **9a** as involving co-ordination of a cyclopentadienylphosphine “bidentate” ligand to the central ruthenium atom. It should be noted that no significant changes have been observed in the ^1H and ^{31}P NMR spectra of **9a** in CD_3CN relative to those in acetone- d_6 , suggesting that the phosphino group, in contrast to the pyridyl group, is tightly bound to the ruthenium atom.

Previously we have reported that an enantiomerically pure sample of the planar-chiral cyclopentadienyl complex (*S*)-[Ru{ η^5 - $\text{C}_5\text{H}_2\text{Me}_2\text{CO}_2\text{C}_{10}\text{H}_{19}$ -(*L*)}{ η^6 - C_6H_6 }] [PF_6^-] (*S*)-**1d** is obtained by fractional recrystallization.⁹ Enantiomer (*R*)-**1d** is also obtained as a (*D*)-menthyl ester analog. Thus, both complexes (*R*)- and (*S*)-**1d** were successfully converted into cyclopentadienylphosphine complexes (*R*)- and (*S*)-**9a** by similar reaction to that of racemic **9a** (Scheme 4). A ^1H NMR experiment using a chiral shift reagent, [Eu(hfc)₃] [hfc = 3-(heptafluoropropylhydroxymethylene)-*D*-camphorate], clearly showed that no racemization of the planar-chiral cyclopentadienyl ligand occurred during the conversion from (*R*)- and (*S*)-**1d** into (*R*)- and (*S*)-**9a**. Therefore, (*R*)- and (*S*)-**9a** showed the same melting points, the same absolute values but with opposite sign in the specific rotations $[\alpha]_D$, and mirror image circular dichroism (CD) spectra in all regions, as depicted in Fig. 2. These results unequivocally suggest that complexes (*R*)- and (*S*)-**9a** are a pair of enantiomers in an optically pure form.

In order to obtain the structural information on the cyclopentadienylphosphine bidentate ligand, we attempted X-ray crystallography of complexes **9a–9d**. However, single crystals did not grow upon recrystallization. Thus we converted the cationic complex into a neutral complex with expectation of good crystallinity. Treatment of **9b** with sodium dithio-

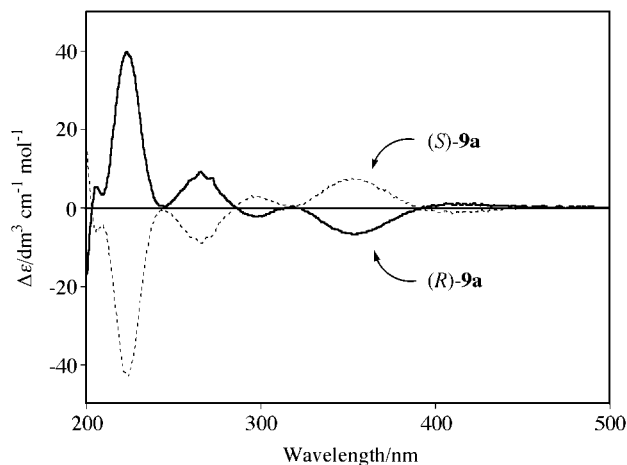
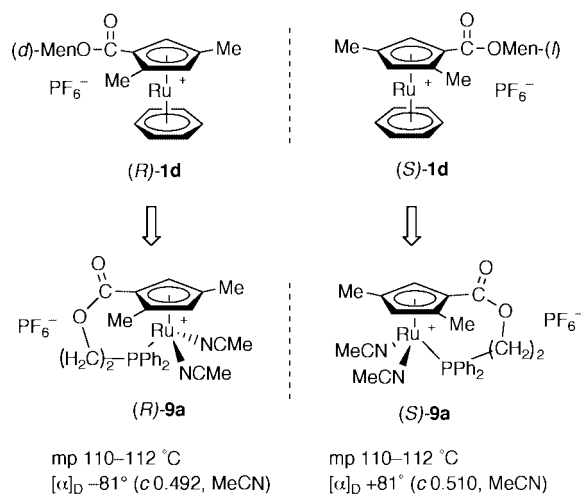
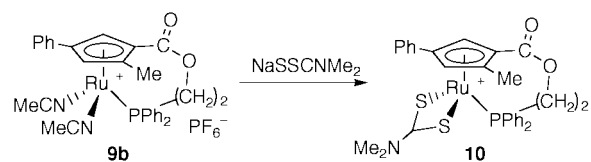


Fig. 2 The CD spectra of complexes (*R*)- and (*S*)-**9a** in acetonitrile.



Scheme 4

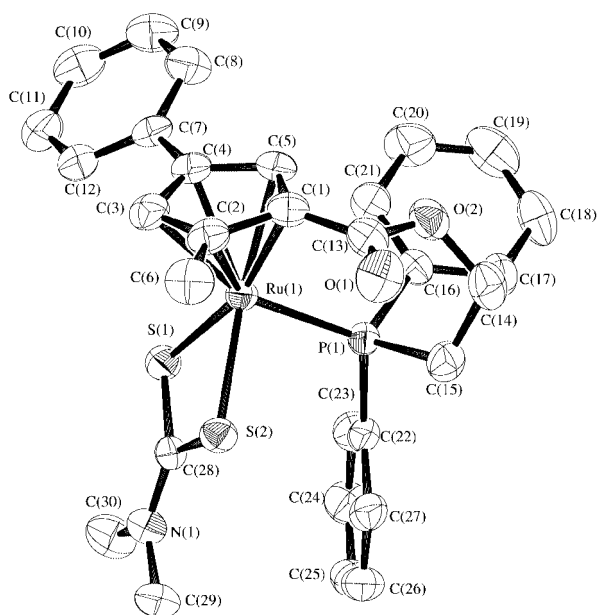


Scheme 5

carbamate in refluxing dichloromethane gave a dithiocarbamate complex, [Ru{ η^5 , η^1 - $\text{C}_5\text{H}_2(\text{Me})(\text{Ph})\text{CO}_2(\text{CH}_2)_2\text{PPh}_2$ }(S_2CNMe_2)] **10**, in 40% yield (Scheme 5).¹⁶ As was expected, good crystals of **10** were obtained by recrystallization from dichloromethane–diethyl ether. The X-ray crystallographic analysis unequivocally showed that **10** has a three-legged piano stool structure with a cyclopentadienylphosphine bidentate ligand. The molecular structure is illustrated in Fig. 3, and selected bond distances and angles are given in Table 1. The structural parameters around the ruthenium atom are similar to those of the non-chelated complex [Ru(η^5 - C_5H_5)(PPh_3)(S_2NMe_2)].^{16,17} The phenyl ring C(7)–C(12) and carbonyl planes defined by C(1), C(13), O(1) and O(2) are slightly twisted relative to the cyclopentadienyl ring, and the torsion angles are 15.8 and 25.8°, respectively. The most striking structural feature of **10** is the conformation of the two phenyl groups on the phosphorus atom. One phenyl group C(22)–C(27) is oriented axially with respect to the plane defined by S(1), S(2) and P(1) and is accommodated on the side of the dithiocarbamate group to minimize the steric repulsion. In contrast, the other phenyl group C(16)–C(21) protrudes equatorially. The phenyl group C(7)–C(12) on the cyclopentadienyl ring also exerts steric

Table 1 Selected bond distances (Å) and angles (°) for [Ru{η⁵,η¹-C₅H₂(Me)(Ph)CO₂(CH₂)₂PPh₂}(S₂CNMe₂)] **10**

| | | | |
|------------------|-----------|------------------|-----------|
| Ru(1)–S(1) | 2.3928(7) | Ru(1)–S(2) | 2.4022(9) |
| Ru(1)–P(1) | 2.3100(7) | Ru(1)–C(1) | 2.163(3) |
| Ru(1)–C(2) | 2.219(3) | Ru(1)–C(3) | 2.233(3) |
| Ru(1)–C(4) | 2.214(3) | Ru(1)–C(5) | 2.170(3) |
| S(1)–C(28) | 1.709(3) | S(2)–C(28) | 1.725(3) |
| N(1)–C(28) | 1.320(4) | N(1)–C(29) | 1.450(4) |
| N(1)–C(30) | 1.460(5) | | |
| | | | |
| S(1)–Ru(1)–S(2) | 72.02(3) | S(1)–Ru(1)–P(1) | 90.92(3) |
| S(1)–Ru(1)–C(1) | 164.99(8) | S(1)–Ru(1)–C(2) | 133.42(8) |
| S(1)–Ru(1)–C(3) | 103.12(8) | S(1)–Ru(1)–C(4) | 101.36(8) |
| S(1)–Ru(1)–C(5) | 130.64(8) | S(2)–Ru(1)–P(1) | 88.20(3) |
| S(2)–Ru(1)–C(1) | 117.44(8) | S(2)–Ru(1)–C(2) | 96.36(8) |
| S(2)–Ru(1)–C(3) | 109.76(8) | S(2)–Ru(1)–C(4) | 146.31(8) |
| S(2)–Ru(1)–C(5) | 156.47(8) | P(1)–Ru(1)–C(1) | 100.69(8) |
| P(1)–Ru(1)–C(2) | 134.64(8) | P(1)–Ru(1)–C(3) | 159.82(8) |
| P(1)–Ru(1)–C(4) | 125.35(8) | P(1)–Ru(1)–C(5) | 96.64(8) |
| Ru(1)–S(1)–C(28) | 89.0(1) | Ru(1)–S(2)–C(28) | 88.33(9) |
| C(28)–N(1)–C(29) | 122.1(3) | C(28)–N(1)–C(30) | 120.8(3) |
| C(29)–N(1)–C(30) | 117.0(3) | S(1)–C(28)–S(2) | 110.3(2) |
| S(1)–C(28)–N(1) | 125.3(2) | S(2)–C(28)–N(1) | 124.3(2) |

**Fig. 3** Molecular structure of complex **10**. Hydrogen atoms are omitted for clarity.

influence on substrates interacting with the ruthenium atom. Therefore, the dithiocarbamate ligand on the ruthenium atom lies in a chiral environment constructed by substituents on the cyclopentadienyl ring and phenyl groups on the phosphorus atom, suggesting that the ruthenium complexes with the tri-substituted cyclopentadienylphosphine bidentate ligands have a great potential applicable to stoichiometric or catalytic asymmetric reactions.

Conclusion

We have developed a convenient synthetic route to planar-chiral cyclopentadienyl-pyridine or -phosphine ruthenium complexes. The phosphino group tightly co-ordinates to the ruthenium atom whereas the pyridyl group dissociates in acetonitrile. The cyclopentadienylphosphine ligand provides a good chiral environment around the ruthenium atom as a result of the steric effect of substituents on the cyclopentadienyl ring and phenyl groups of the phosphine ligand. We are currently investigating application of these complexes as catalysts for asymmetric organic reactions.

Experimental

General considerations

All reactions were carried out under an atmosphere of argon, but the work-up was performed in air. NMR Spectra were measured in CDCl₃ on JEOL JNM-LA400, JNM-LA600 and Bruker ARX400 spectrometers. In ¹H and ¹³C NMR, SiMe₄ was used as an internal standard, and an external 85% H₃PO₄ reference was used for ³¹P NMR. FAB Mass spectra were obtained on a JMS-600H instrument, and IR spectra on a Perkin-Elmer System 2000 FT-IR. Optical rotations and CD spectra were measured on JASCO DIP-1000 and JASCO J-725 instruments, respectively. Elemental analyses were performed by The Material Analysis Center, ISIR, Osaka University. The starting ruthenium complexes [Ru{η⁵-C₅H₂(Me)(R)CO₂R'}(η⁶-C₆H₆)](PF₆) (R = Me, R' = Et **1a**; R = Ph, R' = Et **1b**; R = *t*-Bu, R' = Et **1c**; R = Me, R' = (L)- or (D)-menthyl **1d**) were prepared by a method previously reported.⁹ 2-(Diphenylphosphino)ethanol HO(CH₂)₂PPh₂ was prepared according to the literature method,¹⁴ and 3-(diphenylphosphino)propanol HO(CH₂)₃PPh₂ by a similar method using HO(CH₂)₃Cl in place of HO(CH₂)₂Cl.

Preparations

[Ru{η⁵-C₅H₂Me₂CO₂CH₂C₅H₄N}(η⁶-C₆H₆)](PF₆) **3a.** An acetonitrile solution (50 mL) of [Ru{η⁵-C₅H₂Me₂CO₂Et}(η⁶-C₆H₆)](PF₆) **1a** (1.57 g, 1.1 mmol) was treated with 50 mL of 10% K₂CO₃ aqueous solution under reflux for 1 h. After the reaction mixture was acidified to pH 2–3 with 6 M HCl at 0 °C followed by dilution with acetonitrile the solution was filtered. The solvent was evaporated and the resulting white solid dissolved in 50 mL of dry dichloromethane. After addition of 2 mL of oxalyl chloride and a few drops of DMF, the reaction mixture was stirred at room temperature in the dark for 4 h. Excess of oxalyl chloride and dichloromethane were removed under reduced pressure, and the residue was dissolved in 30 mL of dry acetonitrile. An acetonitrile solution (10 mL) containing 2-pyridylethanol (0.93 mL, 9.6 mmol), triethylamine (1.34 mL, 9.6 mmol) and a catalytic amount of 4-(dimethylamino)pyridine in acetonitrile was added dropwise at 0 °C. The reaction mixture was allowed to warm to room temperature and maintained with stirring overnight. After the solvent was removed under reduced pressure an aqueous solution of NH₄PF₆ was added. Extraction with dichloromethane followed by drying over MgSO₄ and concentration *in vacuo* gave the crude product, which was purified by alumina column chromatography with acetone. Recrystallization from ethanol gave pale yellow crystals (1.74 g, 67%). IR [KBr, $\tilde{\nu}/\text{cm}^{-1}$]: 1732 (CO). ¹H NMR (CDCl₃): δ 8.63 (d, 1 H, *J* = 4.9), 7.82 (dd, 1 H, *J* = 7.9, 6.9), 7.45 (d, 1 H, *J* = 7.9), 7.33 (dd, 1 H, *J* = 4.9, 6.9), 6.08 (s, 6 H), 5.79 (s, 1 H), 5.66 (s, 1 H), 5.45 (d, 1 H, *J* = 12.9), 5.30 (d, 1 H, *J* = 12.9 Hz), 2.28 (s, 3 H) and 2.06 (s, 3 H). FAB MS: *m/z* 468 (M⁺ – PF₆). Calc. for C₂₀H₂₀F₆NO₂PRu: C, 43.49; H, 3.65; F, 20.63; N, 2.54; P, 5.61. Found: C, 43.32; H, 3.57; F, 20.58; N, 2.55; P, 5.58%.

[Ru{η⁵-C₅H₂(Me)(Ph)CO₂CH₂C₅H₄N}(η⁶-C₆H₆)](PF₆) **3b.** This complex was obtained as a pale yellow powder by a method similar to that for **3a** from [Ru{η⁵-C₅H₂(Me)-(Ph)CO₂Et}(η⁶-C₆H₆)](PF₆) **1b** in 70% yield. IR [KBr, $\tilde{\nu}/\text{cm}^{-1}$]: 1737 (CO). ¹H NMR (CDCl₃): δ 8.68 (d, 1 H, *J* = 1.5), 7.89 (m, 1 H), 7.72 (m, 2 H), 7.58 (d, 1 H, *J* = 7.9), 7.41 (m, 4 H), 6.57 (s, 1 H), 6.40 (s, 1 H), 6.29 (s, 6 H), 5.52 (d, 1 H, *J* = 13.5), 5.40 (d, 1 H, *J* = 13.5 Hz) and 2.43 (s, 3 H). FAB MS: *m/z* 170 (M⁺ – PF₆). Calc. for C₂₅H₂₂F₆NO₂PRu: C, 48.87; H, 3.65; F, 18.55; N, 2.28; P, 5.04. Found: C, 48.92; H, 3.41; F, 18.72; N, 2.21; P, 5.10%.

[Ru{η⁵,η¹-C₅H₂Me₂CO₂CH₂C₅H₄N}(CH₃CN)₂](PF₆) **4a.** An acetonitrile solution (50 mL) of complex **3a** (500 mg, 0.91

mmol) was placed in a quartz glass vessel, and irradiated with a 500 W high-pressure mercury lamp for 18 h. Evaporation of the solvents gave a brown solid in quantitative yield. IR [KBr, $\tilde{\nu}/\text{cm}^{-1}$]: 1714 (CO). $^1\text{H NMR}$ (CD_3CN): δ 8.53 (d, 1 H, $J = 5.1$), 7.66 (dd, 1 H, $J = 7.5, 7.4$), 7.41 (d, 1 H, $J = 7.5$), 7.27 (t, 1 H, $J = 7.4, 5.1$), 5.28 (d, 1 H, $J = 1.3$), 5.22 (d, 1 H, $J = 1.3$ Hz), 4.60 (s, 1 H), 4.10 (s, 1 H), 1.95 (s, 3 H) and 1.72 (s, 3 H). Calc. for $\text{C}_{18}\text{H}_{20}\text{F}_6\text{N}_3\text{O}_2\text{PRu}$: C, 38.86; H, 3.62; F, 20.49; N, 7.55; P, 5.57. Found: C, 38.97; H, 3.64; F, 20.90; N, 7.98; P, 5.38%.

[Ru $\{\eta^5, \eta^1\text{-C}_5\text{H}_2(\text{Me})(\text{Ph})\text{CO}_2\text{CH}_2\text{C}_5\text{H}_4\text{N}\}(\text{CH}_3\text{CN})_2\}][\text{PF}_6]$ **4b.** This complex was obtained as a brown powder by a method similar to that for **4a** from **3b** in 99% yield. IR [KBr, $\tilde{\nu}/\text{cm}^{-1}$]: 1715 (CO). $^1\text{H NMR}$ (CD_3CN): δ 8.55 (d, 1 H, $J = 4.9$ Hz), 7.79 (m, 1 H), 7.47 (m, 3 H), 7.33 (m, 4 H), 7.29 (m, 4 H), 5.46 (s, 1 H), 4.79 (s, 1 H), 3.61 (m, 2 H) and 2.06 (s, 3 H). An analytically pure sample was not obtained due to low thermal stability of **4b**.

[Ru $\{\eta^5, \eta^1\text{-C}_5\text{H}_2\text{Me}_2\text{CO}_2\text{CH}_2\text{C}_5\text{H}_4\text{N}\}(\text{bipy})\}][\text{PF}_6]$ **6a.** To a solution of complex **4a** (300 mg, 0.54 mmol) in 20 mL of acetonitrile was added 2,2'-bipyridine (250 mg, 1.62 mmol). The reaction mixture was stirred for 1 h at room temperature. After the solvent was removed *in vacuo*, addition of dichloromethane gave an orange-yellow powder (125 mg, 36%). IR [KBr, $\tilde{\nu}/\text{cm}^{-1}$]: 1694 (CO). $^1\text{H NMR}$ (acetone- d_6): δ 10.10 (d, 1 H, $J = 5.4$), 10.00 (d, 1 H, $J = 6.1$), 9.14 (d, 1 H, $J = 5.1$), 8.55 (d, 1 H, $J = 7.8$), 8.49 (d, 1 H, $J = 8.2$), 8.30 (dd, 1 H, $J = 7.8, 6.8$), 8.20 (dd, 1 H, $J = 7.2, 6.8$), 8.02 (dd, 1 H, $J = 7.1, 6.7$), 7.91 (dd, 1 H, $J = 7.3, 6.7$), 7.82 (dd, 1 H, $J = 7.8, 6.6$), 7.61 (d, 1 H, $J = 8.1$), 7.27 (dd, 1 H, $J = 6.2, 6.3$), 5.72 (d, 1 H, $J = 14.5$), 5.11 (s, 1 H), 4.84 (s, 1 H), 4.55 (d, 1 H, $J = 14.5$ Hz), 1.64 (s, 3 H) and 1.48 (s, 3 H). FAB MS: m/z 485 ($\text{M}^+ - \text{PF}_6$). Calc. for $\text{C}_{24}\text{H}_{22}\text{F}_6\text{N}_3\text{O}_2\text{PRu}$: C, 45.72; H, 3.52; F, 18.08; N, 6.66; P, 4.91. Found: C, 45.56; H, 3.28; F, 18.00; N, 6.57; P, 4.90%.

[Ru $\{\eta^5, \eta^1\text{-C}_5\text{H}_2(\text{Me})(\text{Ph})\text{CO}_2\text{CH}_2\text{C}_5\text{H}_4\text{N}\}(\text{bipy})\}][\text{PF}_6]$ **6b.** This complex was obtained as an orange-yellow powder by a method similar to that for **6a** from **4b** in 99% yield. IR [KBr, $\tilde{\nu}/\text{cm}^{-1}$]: 1693 (CO). $^1\text{H NMR}$ (DMSO- d_6): δ 9.08 (d, 1 H, $J = 5.2$), 8.61 (d, 3 H, $J = 7.6$), 8.18 (t, 1 H, $J = 7.8$), 8.12 (t, 1 H, $J = 7.6$), 8.07 (d, 1 H, $J = 5.6$), 7.88 (t, 1 H, $J = 7.8$), 7.67 (m, 3 H), 7.54 (d, 1 H, $J = 8.3$), 7.40 (m, 5 H), 6.37 (s, 1 H), 5.68 (s, 1 H), 5.43 (d, 1 H, $J = 13.4$), 5.28 (d, 1 H, $J = 13.4$ Hz) and 1.90 (s, 3 H). Calc. for $\text{C}_{29}\text{H}_{24}\text{F}_6\text{N}_3\text{O}_2\text{PRu}$: C, 50.29; H, 3.49; F, 16.46; N, 6.07; P, 4.47. Found: C, 50.08; H, 3.26; F, 16.26; N, 6.29; P, 4.29%.

[Ru $\{\eta^5\text{-C}_5\text{H}_2\text{Me}_2\text{CO}_2(\text{CH}_2)_2\text{PPh}_2\}(\eta^6\text{-C}_6\text{H}_6)\}][\text{PF}_6]$ **8a.** Complex **1a** (538 mg, 1.1 mmol) was dissolved in 20 mL of acetonitrile and treated with 20 mL of 10% K_2CO_3 aqueous solution under reflux for 1 h. The reaction mixture was acidified to pH 2–3 with 6 M HCl at 0 °C and diluted with acetonitrile. After filtration of insoluble compounds the solvent was evaporated. The resulting white solid was dissolved in 20 mL of dry dichloromethane, and 1 mL of oxalyl chloride and a few drops of DMF were added. After being stirred at room temperature in the dark for 4 h, excess of oxalyl chloride and dichloromethane were removed under reduced pressure. The residue was dissolved in 20 mL of dry acetonitrile and a solution containing 2-(diphenylphosphino)ethanol (746 mg, 3.0 mmol), triethylamine (0.42 mL, 3.0 mmol) and a catalytic amount of 4-(dimethylamino)pyridine in acetonitrile was added dropwise at 0 °C. The reaction mixture was allowed to warm to room temperature and maintained with stirring overnight. After removal of acetonitrile under reduced pressure, an aqueous solution of NH_4PF_6 was added and the resulting solution extracted with dichloromethane. The organic layer was dried over MgSO_4 and concentrated *in vacuo*. The crude product was purified by alumina column chromatography with acetone followed by recrystallization from ethanol to give pale yellow

crystals (440 mg, 62%). IR [KBr, $\tilde{\nu}/\text{cm}^{-1}$]: 1721 (CO). $^1\text{H NMR}$ (CDCl_3): δ 7.48–7.43 (m, 4 H), 7.38–7.26 (m, 6 H), 6.08 (s, 6 H), 5.64 (s, 1 H), 5.41 (s, 1 H), 4.47–4.40 (m, 2 H), 2.56–2.50 (m, 2 H), 2.29 (d, 3 H, $J = 2.2$) and 2.25 (d, 3 H, $J = 2.2$ Hz). $^{31}\text{P NMR}$ (CDCl_3): δ -20.89 (s) and -142.67 (sept, $J = 712$ Hz). FAB MS: m/z 529 ($\text{M}^+ - \text{PF}_6$). Calc. for $\text{C}_{28}\text{H}_{28}\text{F}_6\text{O}_2\text{P}_2\text{Ru}$: C, 49.93; H, 4.19; F, 16.92; P, 9.20. Found: C, 49.92; H, 4.08; F, 16.73; P, 9.36%.

[Ru $\{\eta^5\text{-C}_5\text{H}_2(\text{Me})(\text{Ph})\text{CO}_2(\text{CH}_2)_2\text{PPh}_2\}(\eta^6\text{-C}_6\text{H}_6)\}][\text{PF}_6]$ **8b.** This complex was prepared by a method similar to that for **8a** from **1b** in 83% yield. IR [KBr, $\tilde{\nu}/\text{cm}^{-1}$]: 1724 (CO). $^1\text{H NMR}$ (CDCl_3): δ 7.52–7.27 (m, 15 H), 6.26 (s, 1 H), 5.98 (s, 1 H), 5.97 (s, 6 H), 4.54–4.48 (m, 2 H), 2.66–2.50 (m, 2 H) and 2.37 (s, 3 H). $^{31}\text{P NMR}$ (CDCl_3): δ -17.10 (s) and -138.99 (sept, $J_{\text{P-F}} = 708$ Hz). FAB MS: m/z 591 ($\text{M}^+ - \text{PF}_6$). Calc. for $\text{C}_{25}\text{H}_{22}\text{F}_6\text{NO}_2\text{PRu}$: C, 48.87; H, 3.65; F, 18.55; N, 2.28; P, 5.04. Found: C, 48.92; H, 3.41; F, 18.72; N, 2.21; P, 5.10%.

[Ru $\{\eta^5\text{-C}_5\text{H}_2(\text{Me})(t\text{-Bu})\text{CO}_2(\text{CH}_2)_2\text{PPh}_2\}(\eta^6\text{-C}_6\text{H}_6)\}][\text{PF}_6]$ **8c.** This complex was prepared by a method similar to that for **8a** from $[\text{Ru}\{\eta^5\text{-C}_5\text{H}_2(\text{Me})(t\text{-Bu})\text{CO}_2\text{Et}\}(\eta^6\text{-C}_6\text{H}_6)]\text{PF}_6$ **1c** in 75% yield. IR [KBr, $\tilde{\nu}/\text{cm}^{-1}$]: 1715 (CO). $^1\text{H NMR}$ (acetone- d_6): δ 7.60–7.49 (m, 4 H), 7.40 (d, 6 H, $J = 8.3$ Hz), 6.42 (s, 6 H), 5.75 (s, 1 H), 5.68 (s, 1 H), 4.49–4.43 (m, 2 H), 2.70–2.60 (m, 2 H), 2.30 (s, 3 H) and 1.20 (s, 9 H). $^{31}\text{P NMR}$ (acetone- d_6): δ -17.27 (s) and -138.99 (sept, $J_{\text{P-F}} = 708$ Hz). FAB MS: m/z 572 ($\text{M}^+ - \text{PF}_6$). Calc. for $\text{C}_{31}\text{H}_{34}\text{F}_6\text{O}_2\text{P}_2\text{Ru}$: C, 52.03; H, 4.79; F, 15.93; P, 8.66. Found: C, 51.77; H, 4.75; F, 16.00; P, 8.77%.

[Ru $\{\eta^5\text{-C}_5\text{H}_2\text{Me}_2\text{CO}_2(\text{CH}_2)_2\text{PPh}_2\}(\text{C}_6\text{H}_6)\}][\text{PF}_6]$ **8d.** This complex was prepared by a method similar to that of **8a** using 3-(diphenylphosphino)propanol in the place of 2-(diphenylphosphino)ethanol in 48% yield. IR [KBr, $\tilde{\nu}/\text{cm}^{-1}$]: 1732 (CO). $^1\text{H NMR}$ (CDCl_3): δ 7.45–7.34 (m, 10 H), 6.03 (s, 6 H), 5.68 (s, 1 H), 5.65 (s, 1 H), 4.35–4.32 (m, 2 H), 2.25 (s, 3 H), 2.15–2.04 (m, 2 H), 2.04 (s, 3 H) and 1.85 (m, 2 H). $^{31}\text{P NMR}$ (acetone- d_6): δ -11.78 (s) and -144.35 (sept, $J_{\text{P-F}} = 712$ Hz). FAB MS: m/z 543 ($\text{M}^+ - \text{PF}_6$). Calc. for $\text{C}_{29}\text{H}_{30}\text{F}_6\text{O}_2\text{P}_2\text{Ru}$: C, 50.66; H, 4.40; F, 16.58; P, 9.01. Found: C, 50.40; H, 4.21; F, 16.50; P, 9.22%.

[Ru $\{\eta^5, \eta^1\text{-C}_5\text{H}_2\text{Me}_2\text{CO}_2(\text{CH}_2)_2\text{PPh}_2\}(\text{CH}_3\text{CN})\}][\text{PF}_6]$ **9a.** Complex **8a** (230 mg, 0.33 mmol) was placed in a quartz glass vessel and dissolved in 40 mL of acetonitrile. This solution was irradiated with a 500 W high-pressure mercury lamp for 18 h. Evaporation of the solvent gave complex **9a** as a yellow powder in quantitative yield. IR [KBr, $\tilde{\nu}/\text{cm}^{-1}$]: 1715 (CO). $^1\text{H NMR}$ (CDCl_3): δ 7.58–7.45 (m, 5 H), 7.31–7.25 (m, 3 H), 6.90 (t, 2 H, $J = 8.1$), 5.14 (s, 1 H), 5.06–4.97 (m, 1 H), 4.22 (s, 1 H), 3.97–3.90 (m, 1 H), 2.83–2.75 (m, 1 H), 2.57–2.50 (m, 1 H), 2.16 (d, 3 H, $J_{\text{P-H}} = 1.0$), 2.11 (d, 3 H, $J_{\text{P-H}} = 1.2$ Hz), 2.01 (s, 3 H) and 1.84 (s, 3 H). $^{13}\text{C NMR}$ (acetone- d_6): δ 166.52 (s), 135.06 (d, $J_{\text{P-C}} = 38.2$), 133.95 (d, $J_{\text{P-C}} = 12.4$), 131.20 (d, $J_{\text{P-C}} = 2.4$), 130.41 (d, $J_{\text{P-C}} = 8.1$), 130.08 (d, $J_{\text{P-C}} = 42.2$), 129.20 (d, $J_{\text{P-C}} = 1.9$), 128.96 (d, $J_{\text{P-C}} = 10.4$), 127.85 (d, $J_{\text{P-C}} = 12.4$), 126.89 (s), 125.61 (s), 108.17 (s), 98.41 (s), 77.79 (d, $J_{\text{P-C}} = 12.4$), 74.47 (s), 68.81 (s), 59.21 (d, $J_{\text{P-C}} = 3.7$), 17.72 (d, $J_{\text{P-C}} = 30.5$ Hz), 11.70 (s), 11.22 (s), 2.82 (s) and 2.60 (s). $^{31}\text{P NMR}$ (CDCl_3): δ 35.56 (s) and -142.92 (sept, $J_{\text{P-F}} = 712$ Hz). FAB MS: m/z 533 ($\text{M}^+ - \text{PF}_6$). Calc. for $\text{C}_{28}\text{H}_{28}\text{F}_6\text{N}_2\text{O}_2\text{P}_2\text{Ru}$: C, 46.09; H, 4.17; F, 16.32; N, 4.16; P, 9.14. Found: C, 45.87; H, 3.91; F, 16.66; N, 4.30; P, 9.00%.

[Ru $\{\eta^5, \eta^1\text{-C}_5\text{H}_2(\text{Me})(\text{Ph})\text{CO}_2(\text{CH}_2)_2\text{PPh}_2\}(\text{CH}_3\text{CN})\}][\text{PF}_6]$ **9b.** This complex was obtained by a method similar to that for **9a** from **8b** in 99% yield. IR [KBr, $\tilde{\nu}/\text{cm}^{-1}$]: 1723 (CO). $^1\text{H NMR}$ (CDCl_3): δ 7.57–7.26 (m, 13 H), 6.86 (t, 2 H, $J = 8.3$), 5.83 (s, 1 H), 5.30–5.13 (m, 1 H), 4.81 (s, 1 H), 4.15–4.09 (m, 1 H), 2.94–2.85 (m, 1 H), 2.69–2.61 (m, 1 H), 2.27 (d, 3 H, $J_{\text{P-H}} = 1.0$), 2.22 (s, 3 H) and 1.92 (d, 3 H, $J_{\text{P-H}} = 1.5$ Hz). $^{13}\text{C NMR}$ (acetone- d_6):

δ 166.97 (s), 135.58 (d, $J_{\text{P-C}} = 39.0$), 134.78 (d, $J_{\text{P-C}} = 13.0$), 132.19 (d, $J_{\text{P-C}} = 2.6$), 131.21 (d, $J_{\text{P-C}} = 8.5$), 130.73 (d, $J_{\text{P-C}} = 43.0$), 130.14 (d, $J_{\text{P-C}} = 2.5$), 129.97 (s), 129.71 (d, $J_{\text{P-C}} = 10.5$), 129.55 (s), 128.74 (d, $J_{\text{P-C}} = 8.8$), 128.08 (s), 127.32 (s), 110.94 (s), 97.97 (s), 75.88 (d, $J_{\text{P-C}} = 12.5$), 73.90 (s), 69.53 (s), 60.32 (d, $J_{\text{P-C}} = 3.8$), 18.37 (d, $J_{\text{P-C}} = 30.7$ Hz), 12.35 (s), 3.76 (s) and 3.06 (s). ^{31}P NMR (CDCl_3): δ 35.19 (s) and -144.37 (sept, $J_{\text{P-F}} = 712$ Hz). Calc. for $\text{C}_{31}\text{H}_{30}\text{F}_6\text{N}_2\text{O}_2\text{P}_2\text{Ru}$: C, 50.34; H, 4.09; F, 15.41; N, 3.79; P, 8.38. Found: C, 50.36; H, 4.60; F, 15.33; N, 3.85; P, 8.32%.

[Ru $\{\eta^5, \eta^1\text{-C}_5\text{H}_2(\text{Me})(t\text{-Bu})\text{CO}_2(\text{CH}_2)_2\text{PPh}_2\}(\text{CH}_3\text{CN})_2\}\text{[PF}_6\text{]}]$ **9c. This complex was obtained by a method similar to that for **9a** from **8c** in 99% yield. IR [KBr, $\tilde{\nu}/\text{cm}^{-1}$]: 1727 (CO). ^1H NMR (CDCl_3): δ 7.94–7.70 (m, 2 H), 7.56–7.48 (m, 3 H), 7.42–7.35 (m, 3 H), 7.06 (t, 2 H, $J = 8.1$), 5.18 (d, 1 H, $J = 1.7$), 5.05–4.96 (m, 1 H), 4.46 (d, 1 H, $J = 1.7$), 3.93–3.87 (m, 1 H), 2.89–2.81 (m, 1 H), 2.57–2.50 (m, 1 H), 2.18 (d, 3 H, $J_{\text{P-H}} = 1.0$), 2.16 (d, 3 H, $J_{\text{P-H}} = 1.5$ Hz), 2.06 (s, 3 H) and 1.26 (s, 9 H). ^{13}C NMR (acetone- d_6): δ 167.61 (s), 134.42 (d, $J_{\text{P-C}} = 38.9$), 134.13 (d, $J_{\text{P-C}} = 12.5$), 131.04 (d, $J_{\text{P-C}} = 2.0$), 130.96 (d, $J_{\text{P-C}} = 8.5$), 130.56 (d, $J_{\text{P-C}} = 40.9$), 129.32 (d, $J_{\text{P-C}} = 1.9$), 128.51 (d, $J_{\text{P-C}} = 10.1$), 127.78 (d, $J_{\text{P-C}} = 8.73$), 125.86 (s), 117.47 (s), 104.90 (s), 73.66 (d, $J_{\text{P-C}} = 12.1$), 71.51 (s), 67.08 (s), 59.75 (d, $J_{\text{P-C}} = 3.2$), 31.30 (s), 29.69 (s), 19.06 (d, $J_{\text{P-C}} = 30.3$ Hz), 11.62 (s), 2.89 (s) and 2.69 (s). ^{31}P NMR (CDCl_3): δ 31.4 (s) and -144.4 (sept, $J_{\text{P-F}} = 712$ Hz). FAB MS: m/z 576 ($\text{M}^+ - \text{PF}_6$). Calc. for $\text{C}_{29}\text{H}_{34}\text{F}_6\text{N}_2\text{O}_2\text{P}_2\text{Ru}$: C, 48.61; H, 4.36; F, 15.91; N, 3.91; P, 8.64. Found: C, 48.46; H, 4.63; F, 15.69; N, 3.71; P, 8.56%.**

[Ru $\{\eta^5, \eta^1\text{-C}_5\text{H}_2\text{Me}_2\text{CO}_2(\text{CH}_2)_3\text{PPh}_2\}(\text{CH}_3\text{CN})_2\}\text{[PF}_6\text{]}]$ **9d. This complex was prepared by a method similar to that for **9a** from **8d** in quantitative yield. IR [KBr, $\tilde{\nu}/\text{cm}^{-1}$]: 1713 (CO). ^1H NMR (CDCl_3): δ 7.51–7.23 (m, 10 H), 5.10 (s, 1 H), 4.94 (s, 1 H), 4.95–4.87 (m, 1 H), 3.77–3.72 (m, 1 H), 2.96–2.93 (m, 1 H), 2.72–2.68 (m, 1 H), 2.19 (d, 3 H, $J_{\text{P-H}} = 1.5$), 2.12 (s, 3 H), 2.10 (d, 3 H, $J_{\text{P-H}} = 1.2$ Hz) and 1.71 (s, 3 H). ^{31}P NMR (CDCl_3): δ 43.53 (s) and -144.35 (sept, $J_{\text{P-F}} = 712$ Hz). FAB MS: m/z 547 ($\text{M}^+ - \text{PF}_6$). Calc. for $\text{C}_{27}\text{H}_{30}\text{F}_6\text{N}_2\text{O}_2\text{P}_2\text{Ru}$: C, 46.89; H, 4.37; F, 16.48; N, 4.05; P, 8.96. Found: C, 46.69; H, 4.29; F, 16.55; N, 4.18; P, 9.02%.**

(S)-[Ru $\{\eta^5, \eta^1\text{-C}_5\text{H}_2\text{Me}_2\text{CO}_2(\text{CH}_2)_2\text{PPh}_2\}(\text{CH}_3\text{CN})_2\}\text{[PF}_6\text{]}]$ **(S)-9a. This complex was prepared from (S)-[Ru $\{\eta^1\text{-C}_5\text{H}_2\text{Me}_2\text{CO}_2\text{C}_{10}\text{H}_{19}\text{-}(L)(\eta^6\text{-C}_6\text{H}_6)\}\text{[PF}_6\text{]}]$ **1d** as described for the preparation of racemic **9a**. Spectroscopic data of (S)-**9a** are the same as those of racemic **9a** within experimental error. Calc. for $\text{C}_{28}\text{H}_{28}\text{F}_6\text{N}_2\text{O}_2\text{P}_2\text{Ru}$: C, 46.09; H, 4.17; F, 16.32; N, 4.16; P, 9.14. Found: C, 45.90; H, 3.82; F, 16.57; N, 4.00; P, 9.30%.**

(R)-[Ru $\{\eta^5, \eta^1\text{-C}_5\text{H}_2\text{Me}_2\text{CO}_2(\text{CH}_2)_2\text{PPh}_2\}(\text{CH}_3\text{CN})_2\}\text{[PF}_6\text{]}]$ **(R)-9a. This complex was prepared from (R)-**1d** as described for the preparation of racemic **9a**. Spectroscopic data of (R)-**9a** are the same as those of racemic **9a** within experimental error. Calc. for $\text{C}_{28}\text{H}_{28}\text{F}_6\text{N}_2\text{O}_2\text{P}_2\text{Ru}$: C, 46.09; H, 4.17; F, 16.32; N, 4.16; P, 9.14. Found: C, 45.80; H, 4.06; F, 16.90; N, 4.25; P, 9.09%.**

[Ru $\{\eta^5, \eta^1\text{-C}_5\text{H}_2(\text{Me})(\text{Ph})\text{CO}_2(\text{CH}_2)_2\text{PPh}_2\}(\text{S}_2\text{CNMe}_2)\text{]}]$ **10. To a stirred solution of complex **9b** (300 mg, 0.41 mmol) in 30 mL of dichloromethane was added sodium dithiocarbamate (64 mg, 0.45 mmol). After being stirred under reflux for 2 h, the solvent was removed under reduced pressure. The residue was purified by alumina column chromatography using dichloromethane–hexane (1:1 v/v) as eluent. Recrystallization from dichloromethane–ether gave orange-yellow crystals (104 mg, 40%). IR [KBr, $\tilde{\nu}/\text{cm}^{-1}$]: 1695 (CO). ^1H NMR (acetone- d_6): δ 7.61–7.57 (m, 4 H), 7.50–7.30 (m, 6 H), 7.10–7.04 (m, 3 H), 6.86 (t, 2 H, $J = 8.1$ Hz), 5.32 (s, 1 H), 5.13–5.03 (m, 1 H), 4.90 (s, 1 H), 4.10–4.02 (m, 1 H), 2.64 (s, 3 H), 2.47 (s, 3 H) and 2.28 (s, 3 H). ^{13}C NMR (CDCl_3): δ 212.56 (s), 166.98 (s), 135.51 (s),**

Table 2 Crystallographic data for [Ru $\{\eta^5, \eta^1\text{-C}_5\text{H}_2(\text{Me})(\text{Ph})\text{CO}_2(\text{CH}_2)_2\text{PPh}_2\}(\text{S}_2\text{CNMe}_2)\text{]}]$ **10**

| | |
|------------------------|--|
| Chemical formula | $\text{C}_{30}\text{H}_{30}\text{NO}_2\text{PRuS}_2$ |
| Formula weight | 632.74 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ (no. 2) |
| $a/\text{\AA}$ | 12.346(3) |
| $b/\text{\AA}$ | 12.759(4) |
| $c/\text{\AA}$ | 9.569(2) |
| $\alpha/\text{^\circ}$ | 105.55(2) |
| $\beta/\text{^\circ}$ | 91.92(2) |
| $\gamma/\text{^\circ}$ | 105.01(3) |
| $V/\text{\AA}^3$ | 1393.9(7) |
| Z | 2 |
| μ/cm^{-1} | 7.98 |
| Total data collected | 6678 |
| Unique data | 6393 ($R_{\text{int}} = 0.017$) |
| Observed data | 5452 ($I > 3.0\sigma(I)$) |
| R | 0.032 |
| R' | 0.045 |

134.61 (d, $J_{\text{P-C}} = 38.0$), 134.09 (d, $J_{\text{P-C}} = 37.1$), 133.26 (d, $J_{\text{P-C}} = 7.4$), 130.64 (br), 128.76 (s), 128.67 (d, $J_{\text{P-C}} = 10.0$), 127.79 (s), 127.27 (s), 125.40 (d, $J_{\text{P-C}} = 8.5$), 106.40 (s), 95.13 (s), 76.84 (s), 76.32 (d, $J_{\text{P-C}} = 14.6$), 72.29 (s), 59.10 (s), 38.30 (s), 19.79 (d, $J_{\text{P-C}} = 27.9$ Hz) and 13.86 (s). ^{31}P NMR (acetone- d_6): δ 47.55 (s). FAB MS: m/z 633 (M^+). Calc. for $\text{C}_{30}\text{H}_{30}\text{NO}_2\text{PRuS}_2$: C, 56.95; H, 4.78; N, 2.20; P, 4.89; S, 10.13. Found: C, 56.68; H, 4.64; N, 2.50; P, 4.73; S, 10.09%.

X-Ray diffraction analysis for complex 10

Crystals suitable for X-ray diffraction were mounted on a glass fiber with epoxy resin. All measurements were performed on a Rigaku AFC5R automated four circle diffractometer using graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71069$ Å) at 23 °C. Three standard reflections were monitored at every 150 and no decay was observed. An empirical absorption correction was made by the ψ -scan technique.

The structure was solved by Patterson methods (DIRDIF 94 Patty).¹⁸ All non-hydrogen atoms were refined anisotropically by full-matrix least-squares minimizing $\sum w(|F_o| - |F_c|)^2$. The hydrogen atoms were included at the calculated positions ($d\text{C-H} = 0.95$ Å) and their parameters not refined. All calculations were performed using the TEXSAN crystallographic software package.¹⁹ Crystallographic data are listed in Table 2.

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References

- S. G. Davies, *Organotransition Metal Chemistry: Applications to Organic Synthesis*, Pergamon, Oxford, 1982; I. Ojima (Editor), *Catalytic Asymmetric Synthesis*, VCH, New York, 1993; R. Noyori, *Asymmetric Catalysis in Organic Synthesis*, Wiley, New York, 1994.
- For reviews, see: H. Brunner, *Adv. Organomet. Chem.*, 1980, **18**, 151; G. Consiglio and F. Morandini, *Chem. Rev.*, 1987, **87**, 761; R. L. Halterman, *Chem. Rev.*, 1992, **92**, 965; H. Brunner, *Angew. Chem., Int. Ed.*, 1999, **38**, 1195.
- W. A. Schenk and M. Dürr, *Chem. Eur. J.*, 1997, **3**, 713; W. A. Schenk, J. Frisch, M. Dürr, N. Burzlaff, D. Stalke, R. Fleischer, W. Adam, F. Precht and A. K. Smerz, *Inorg. Chem.*, 1997, **36**, 2372; A. J. Davenport, D. L. Davies, J. Fawcett, S. A. Garratt, L. Lad and D. R. Russell, *Chem. Commun.*, 1997, 2347; D. Carmona, F. J. Lahoz, S. Elipe, L. A. Oro, M. P. Lamata, F. Viguri, C. Mir, C. Cativiela and M. P. L.-R. de Viu, *Organometallics*, 1998, **17**, 2986; E. P. Küding, C. M. Sauden and G. Bernardinelli, *Angew. Chem., Int. Ed.*, 1999, **38**, 1220.

- 4 H. Brunner, K. Fisch, P. G. Jones and J. Salbeck, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1521; S. G. Davies, *Aldrichchim. Acta*, 1990, **23**, 31; M. Brookhart, Y. Liu, E. W. Goldman, D. A. Timmers and G. D. Williams, *J. Am. Chem. Soc.*, 1991, **113**, 927; J. W. Faller, M. R. Mazzieri, J. T. Nguyen, J. Parr and M. Tokunaga, *Pure Appl. Chem.*, 1994, **66**, 1463; J. A. Gladysz and B. J. Boone, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 550.
- 5 For reviews, see: H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R. M. Waymouth, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1143; A. L. McKnight and R. M. Waymouth, *Chem. Rev.*, 1998, **98**, 2587.
- 6 Y. Kataoka, Y. Saito, K. Nagata, K. Kitamura, A. Shibahara and K. Tani, *Chem. Lett.*, 1995, 833; Y. Kataoka, Y. Saito, A. Shibahara and K. Tani, *Chem. Lett.*, 1997, 621; T. A. Mobley and R. G. Bergman, *J. Am. Chem. Soc.*, 1998, **120**, 3253; Y. Kataoka, A. Shibahara, Y. Saito, T. Yamagata and K. Tani, *Organometallics*, 1998, **17**, 4338; B. M. Trost, B. Vidal and M. Thommen, *Chem. Eur. J.*, 1999, **5**, 1055.
- 7 J. C. Ruble and G. C. Fu, *J. Org. Chem.*, 1996, **61**, 7230; P. I. Dosa, J. C. Ruble and G. C. Fu, *J. Org. Chem.*, 1997, **62**, 444; J. C. Ruble, H. A. Latham and G. C. Fu, *J. Am. Chem. Soc.*, 1997, **119**, 1492; J. C. Ruble, J. Tweddell and G. C. Fu, *J. Org. Chem.*, 1998, **63**, 2794; M. M.-C. Lo and G. C. Fu, *J. Am. Chem. Soc.*, 1998, **120**, 10270; J. C. Ruble and G. C. Fu, *J. Am. Chem. Soc.*, 1998, **120**, 11532; B. L. Hodous, J. C. Ruble and G. C. Fu, *J. Am. Chem. Soc.*, 1999, **121**, 2637.
- 8 M. Uno, K. Ando, N. Komatsuzaki and S. Takahashi, *J. Chem. Soc., Chem. Commun.*, 1992, 964; M. Uno, K. Ando, N. Komatsuzaki, T. Tanaka, M. Sawada and S. Takahashi, *J. Chem. Soc., Chem. Commun.*, 1993, 1549; M. Uno, N. Komatsuzaki, K. Shirai and S. Takahashi, *J. Organomet. Chem.*, 1993, **462**, 343; M. Uno, K. Ando, N. Komatsuzaki, T. Tsuda, T. Tanaka, M. Sawada and S. Takahashi, *J. Organomet. Chem.*, 1994, **473**, 303; N. Komatsuzaki, M. Uno, K. Shirai, T. Tanaka, M. Sawada and S. Takahashi, *J. Organomet. Chem.*, 1995, **498**, 53; M. Uno, K. Shirai, K. Ando, N. Komatsuzaki, T. Tanaka, M. Sawada and S. Takahashi, *Chem. Lett.*, 1995, 7; Y. Morimoto, K. Ando, M. Uno and S. Takahashi, *Chem. Commun.*, 1997, 1795; T. Katayama, Y. Morimoto, M. Yuge, M. Uno and S. Takahashi, *Organometallics*, 1999, **18**, 3087.
- 9 N. Komatsuzaki, M. Uno, H. Kikuchi and S. Takahashi, *Chem. Lett.*, 1996, 677.
- 10 For reviews, see: P. Jutzi and U. Siemeling, *J. Organomet. Chem.*, 1995, **500**, 175; P. Jutzi and T. Redeker, *Eur. J. Inorg. Chem.*, 1998, 663.
- 11 B. Thierrien and T. R. Ward, *Angew. Chem., Int. Ed.*, 1999, **38**, 405; B. Thierrien, A. König and T. R. Ward, *Organometallics*, 1999, **18**, 1565.
- 12 T. P. Gill and K. R. Mann, *Organometallics*, 1982, **1**, 485.
- 13 T. Ohnishi, Y. Miyaki, H. Asano and H. Kurosawa, *Chem. Lett.*, 1999, 809; B. Thierrien, T. R. Ward, M. Pilkington, C. Hoffmann, F. Gilardoni and J. Weber, *Organometallics*, 1998, **17**, 330.
- 14 D. Cantreux, J. Gamet, R. Jacquier and J. Verducci, *Tetrahedron*, 1984, **40**, 3087.
- 15 S. G. Davies, J. P. Macnally and A. J. Smallridge, *Adv. Organomet. Chem.*, 1990, **30**, 1.
- 16 Q. J. McCubbin, F. J. Stoddart, T. Welton, A. J. P. White and D. J. Williams, *Inorg. Chem.*, 1998, **37**, 3753.
- 17 A. W. Cordes and M. Draganjac, *Acta Crystallogr., Sect. C*, 1988, **44**, 363.
- 18 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, DIRDIF 92, Technical Report of the Crystallographic Laboratory, University of Nijmegen, 1994.
- 19 TEXSAN, Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985 and 1992.

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