Synthesis and Characterization of Ruthenium(II) Complexes Containing Chiral Bis(ferrocenyl)−P_3 or −P_2S Ligands. Asymmetric Transfer Hydrogenation of Acetophenone

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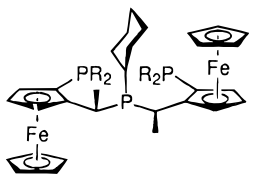
A number of new chiral bis(ferrocenyl)−triphosphine ligands have been synthesized by the reaction of cyclohexylphosphine with different chiral ferrocenyl aminophosphines in hot acetic acid. The thioether ligand bis{(*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl} sulfide has been similarly prepared by the reaction of (*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]-ethyl acetate with either (*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl mercaptan or (*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl mercaptan sodium salt. All the above reactions proceed with retention of configuration on the side-chain stereocenters of the starting materials. Monomeric Ru(II) complexes containing either chloride or acetonitrile coligands have been prepared with all the chiral tridentate ligands. Both the new ligands and the ruthenium complexes have been characterized by multinuclear NMR spectroscopy. The structure of [(*S*)-(*R*)-Pigiphos]$RuCl_2 \cdot 2CH_2Cl_2$ ((*S*)-(*R*)-Pigiphos = bis{(*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl}cyclohexylphosphine) has been determined by X-ray diffraction. The asymmetric transfer hydrogenation of acetophenone catalyzed by various Ru(II) bis(ferrocenyl) tridentate complexes in propan-2-ol is also reported.

Introduction

Asymmetric catalysis by means of soluble transition-metal complexes makes extensive use of chiral chelating diphosphines, as the carrier of the chiral information.[1] Such ligands very often also display C_2 symmetry, this particular aspect being advantageous for a metal center adopting a square-planar coordination geometry.[2] On the other hand, chiral ferrocenyl diphosphines are asymmetric and are recognized as one of the most important classes of auxiliaries used in asymmetric catalysis. Since the pioneering work of Hayashi and co-workers,[3] the range of application of such ligands has been steadily growing and recently culminated in two industrial asymmetric hydrogenation processes.[4]

A most important feature of ferrocenyl ligands is their synthetic versatility, allowing a great variety of ligand fragments to be assembled into a single common structural framework.[5] As an extension of the general synthetic concept adopted for the preparation of bidentate ligands, we recently reported the synthesis and characterization of the tridentate bis(ferrocenyl) ligand Pigiphos.[6]



(*S*)-(*R*)-Pigiphos

Recognizing that chiral triphosphines have so far been rather neglected in asymmetric catalysis,[7] we are currently pursuing a systematic study of ligands of the Pigiphos type, their coordination chemistry, and possible applications in asymmetric catalysis.

Herein we report the synthesis and characterization of a series of Ru(II) complexes containing Pigiphos-type

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ligands. Preliminary results in the asymmetric transfer hydrogenation of acetophenone catalyzed by various Ru(II) bis(ferrocenyl) tridentate complexes in propan-2-ol are also reported.

Experimental Section

General Information. All manipulations were performed under a pure nitrogen atmosphere unless otherwise stated. Freshly distilled, dry solvents were used throughout. Bis[3,5-bis(trifluoromethyl)phenyl]chlorophosphine, bis(3,5-dimethylphenyl)chlorophosphine, and bis[3-(trifluoromethyl)phenyl]-chlorophosphine were prepared by literature methods.[8] (*S*)-(*R*)-PPFA (**1**),[9] (*R*)-*N*,*N*-dimethyl-1-[(*S*)-2-(dicyclohexylphosphino)ferrocenyl]ethylamine (**3**),[10] (*R*)-*N*,*N*-dimethyl-1-{(*S*)-2-[bis(3,5-dimethylphenyl)phosphino]ferrocenyl}ethylamine (**5**),[9] (*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl acetate (**6**),[9] (*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl mercaptan (**7**),[11] and bis{(*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl}-cyclohexylphosphine ((*S*)-(*R*)-Pigiphos, **8**)[6] were prepared as previously described. $RuCl_2(PPh_3)_3$,[12] $[Ru_2(CF_3CO_2)_4(COD)_2H_2O]$,[13] $RuCl_2(DMSO)_4$,[14] and $[Ru(NBD)(CH_3CN)_4](BF_4)_2$[15] were synthesized as previously reported. Cyclohexylphosphine, dicyclohexylchlorophosphine, and *m*-bromobenzotrifluoride were obtained from Strem. All of the other chemicals were commercial products and were used as received. The solid compounds were collected on sintered-glass frits before being dried under a stream of nitrogen. ^{31}P NMR spectra were recorded on a Bruker Avance DRX-500 spectrometer operating at 202.47 MHz. Chemical shifts are relative to external 85% H_3PO_4, with downfield values reported as positive. ^1H and ^{13}C NMR spectra were recorded at 500.13 and 125.76 MHz, respectively, on a Bruker Avance DRX-500 spectrometer equipped with a variable-temperature control unit accurate to ±0.1 °C. Chemical shifts are relative to tetramethylsilane as external reference or are calibrated against solvent resonances. ^{19}F NMR spectra were recorded at 282.28 MHz on a Varian VXR 300 spectrometer. Chemical shifts are relative to $CFCl_3$ as external reference, with upfield shifts reported as negative. The assignments of the signals resulted from ^1H homonuclear decoupling experiments and proton-detected ^1H,^{13}C and ^1H,^{31}P correlations using degassed nonspinning samples. 2D NMR spectra were recorded using pulse sequences suitable for phase-sensitive representations with TPPI. The ^1H,^{13}C correlations[16] were recorded using the standard HMQC sequence with no decoupling during acquisition; 1024 increments of size 2K (with 32 scans each) were collected covering the full range in both dimensions (ca. 5000 Hz in F_2 and ca. 18 000 Hz in F_1) with a relaxation delay of 0.8 s. The ^1H,^{31}P correlations[17] were recorded using the standard HMQC sequence with no decoupling during acquisition; 512 increments of size 2K (with 16 scans each) were collected, which covered the full range in both dimensions (ca. 5000 Hz in F_2 and ca. 15 000 Hz in F_1) with a relaxation delay of 1.0 s. Infrared spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer using samples mulled in Nujol between KBr plates. Merck silica gel 60, 230−400 mesh ASTM, was used for column chromatography. Thin-layer chromatography was performed with Macherey-Nagel Polygram SIL G/UV254 precoated plastic sheets. Optical rotations were measured with a Perkin-Elmer 341 polarimeter using 10 cm cells. GC analyses were performed on a Shimadzu GC-14A gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μm FT) SPB-1 Supelco fused silica capillary column and coupled with a C-R6A Chromatopac operating in the corrected area method. Enantiomeric excesses (ee's) were determined by GC analyses on a Shimadzu GC-17A gas chromatograph equipped with a flame ionization detector and a 40 m × 0.25 mm i.d. Chiraldex G-TA capillary column and coupled with a Shimadzu C-R7A Chromatopac. Conductivities were measured with a Model 990101 Orion conductance cell connected to a Model 101 conductivity meter.

Synthesis of the Ferrocenyl Aminophosphines. (*S*)-*N*,*N*-Dimethyl-1-[(*R*)-2-{bis[3,5-bis(trifluoromethyl)phenyl]-phosphino}ferrocenyl]ethylamine ((*S*)-(*R*)-4-CF_3-PPFA, 2). *sec*-Butyllithium (10 mL, 16.0 mmol, 1.6 M in hexane) was added to a solution of (*S*)-*N*,*N*-dimethyl-1-ferrocenylethylamine (3.1 g, 11.8 mmol) in diethyl ether (50 mL), and the mixture was stirred at room temperature overnight. Bis[3,5-bis-(trifluoromethyl)phenyl]chlorophosphine (6.2 g, 11.8 mmol) in diethyl ether (10 mL) was added dropwise. After the resulting solution was refluxed for 5 h, a saturated aqueous solution of $NaHCO_3$ was added. The organic phase was separated, and the aqueous phase was washed twice with diethyl ether (2 × 100 mL). The ether extracts were collected together and dried over Na_2SO_4. After the solvent was evaporated in vacuo, the brown oil obtained was dissolved in *n*-pentane (5 mL) and this solution was filtered and chromatographed over aluminum oxide using *n*-hexane−EtOAc (25:1) as eluent (R_f 0.65). Pure **2** was obtained in 91.8% yield as a viscous red-brown oil which solidified at −20 °C. $[\alpha]^{25}_D = +222.0$. ^{31}P NMR ($CDCl_3$, 294 K): δ −19.27 (s). ^1H NMR ($CDCl_3$, 294 K): δ 4.15 (qd, 1H, C*H*CH$_3$, $J_{HH} = 6.7$ Hz, $J_{HP} = 2.4$ Hz), 3.63 (m, 1H, Cp *H*), 4.40 (t, 1H, Cp *H*), 4.51 (m, 1H, Cp *H*), 4.02 (s, 5H, C_5H_5), 1.23 (d, 3H, CH_3), 1.72 (s, 6H, N(CH_3)$_2$), 7.55−7.65 (m, 2H, Ph *H*), 7.73 (s, 1H, Ph *H*), 7.90−8.05 (m, 3H, Ph *H*). Anal. Calcd for $C_{30}H_{24}NF_{12}FeP$: C, 50.55; H, 3.39; N, 1.96. Found: C, 50.81; H, 3.44; N, 1.84.

(*R*)-*N*,*N*-Dimethyl-1-{(*S*)-2-[bis(3-(trifluoromethyl)-phenyl)phosphino]ferrocenyl}ethylamine ((*R*)-(*S*)-2-CF_3-PPFA, 4). An improved synthesis of a reported procedure[18] was employed: *sec*-Butyllithium (7.0 mL, 9.1 mmol, 1.3 M in cyclohexane) was added to a solution of (*R*)-*N*,*N*-dimethyl-1-ferrocenylethylamine (2.13 g, 8.3 mmol) in diethyl ether (50 mL), and the mixture was stirred at room temperature for 2.5 h. Bis[3-(trifluoromethyl)phenyl]chlorophosphine (2.1 mL, 8.3 mmol) in diethyl ether (50 mL) was then added dropwise. After the resulting solution was refluxed for 5 h, a saturated aqueous solution of $NaHCO_3$ was added. The organic phase was separated, and the aqueous phase was washed twice with diethyl ether (2 × 100 mL). The ether extracts were collected together and dried over Na_2SO_4. The solvent was removed in vacuo to give a red oil, which was chromatographed over silica using 2% triethylamine in diethyl ether as eluent (R_f 0.80). The residue obtained was purified by short-column chromatography (silica, *n*-hexane−EtOAc (3:1)) to give the pure product as a red viscous oil (42% yield). Anal. Calcd for $C_{28}H_{26}NF_6FeP$: C, 58.30; H, 4.54; N, 2.43. Found: C, 58.24; H, 4.61; N, 2.33.

Synthesis of the Chiral Bis(ferrocenyl) Triphosphine Ligands. Bis[(*R*)-1-{(*S*)-2-[bis(3,5-dimethylphenyl)-

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phosphino]ferrocenyl}ethyl]cyclohexylphosphine ((*R*)-(*S*)-8-Me-Pigiphos, 9). Cyclohexylphosphine (200 μL, 1.51 mmol) was added to a solution of (*R*)-*N*,*N*-dimethyl-1-{(*S*)-2-[bis(3,5-dimethylphenyl)phosphino]ferrocenyl}ethylamine (**5**; 1.50 g, 3.02 mmol) in acetic acid (15 mL), and the mixture was stirred at 70 °C for 6.5 h. The solvent was removed at 65 °C in vacuo, and the residue was crystallized from CH_2Cl_2/MeOH to give orange microcrystals of pure **9** (520 mg, 34% yield). $[\alpha]^{25}_D = -293.4$. ^{1}H NMR ($CDCl_3$, 294 K): δ 3.18 (qd, 1H, CH^{I}CH$_3$, $J_{HH} = 7.0$ Hz, $J_{HP} = 2.7$ Hz), 2.80 (qntd, 1H, CH^{II}CH$_3$, $J_{HH} = J_{HP} = 7.1$ Hz, $J_{HP} = 3.1$ Hz), 1.61 (t, 3H, CH^{I}CH_3), 1.56 (dd, 3H, CH^{II}CH_3, $J_{HP} = 5.5$ Hz), 4.32 (m, 1H, Cp H^{I}), 4.24 (t, 1H, Cp H^{II}), 4.10 (m, 1H, Cp H^{III}), 4.07 (t, 1H, Cp H^{IV}), 4.00 (m, 1H, Cp H^{V}), 3.90 (m, 1H, Cp H^{VI}), 3.93 (s, 5H, C$_5H_5^{I}$), 3.86 (s, 5H, C$_5H_5^{II}$), 2.41 (s, 6H, Ph CH_3), 2.37 (s, 6H, Ph CH_3), 2.32 (s, 6H, Ph CH_3), 2.27 (s, 6H, Ph CH_3). ^{13}C NMR ($CDCl_3$, 294 K): δ 26.5 (CH^{I}CH$_3$), 25.4 (CH^{II}CH$_3$), 22.2 (CH^{I}CH_3), 18.1 (CH^{II}CH_3), 70.6 (*C*p H^{I}), 68.3 (*C*pH^{II}), 71.3 (*C*pH^{III}), 68.0 (*C*p H^{V}), 71.6 (*C*p H^{V}), 71.1 (*C*p H^{VI}), 69.8 (s, 5H, C$_5H_5^{I}$), 69.7 (s, 5H, C$_5H_5^{II}$). Anal. Calcd for $C_{62}H_{71}Fe_2P_3$: C, 72.92; H, 7.01. Found: C, 72.88; H, 7.22.

Bis[(*R*)-1-{(*S*)-2-[bis(3-(trifluoromethyl)phenyl)-phosphino]ferrocenyl}ethyl]cyclohexylphosphine ((*R*)-(*S*)-4-CF$_3$-Pigiphos, 10). Cyclohexylphosphine (190 μL, 1.44 mmol) was added to a solution of (*R*)-(*S*)-2-CF$_3$-PPFA (1.66 g, 2.88 mmol) in acetic acid (15 mL), and the mixture was stirred at 75 °C for 32 h. The solvent was removed at 75 °C in vacuo, and the residue was chromatographed over silica using *n*-hexane−EtOAc (20:1) as eluent (R_f 0.22) to give pure **10** in 46% yield. $[\alpha]^{25}_D = -284.5$. ^{1}H NMR ($CDCl_3$, 294 K): δ 3.19 (qd, 1H, CH^{I}CH$_3$, $J_{HH} = 7.0$ Hz, $J_{HP} = 1.7$ Hz), 2.86 (qntd, 1H, CH^{II}CH$_3$, $J_{HH} = J_{HP} = 7.1$ Hz, $J_{HP} = 2.6$ Hz), 1.65 (t, 3H, CH^{I}CH_3), 1.58 (dd, 3H, CH^{II}CH_3, $J_{HP} = 5.6$ Hz), 4.35 (t, 1H, Cp H^{I}), 4.33 (m, 1H, Cp H^{II}), 4.14 (t, 1H, Cp H^{III}), 4.11 (m, 1H, Cp H^{IV}), 3.97 (m, 1H, Cp H^{V}), 3.87 (m, 1H, Cp H^{VI}), 3.92 (s, 5H, C$_5H_5^{I}$), 3.89 (s, 5H, C$_5H_5^{II}$). ^{13}C NMR ($CDCl_3$, 294 K): δ 26.7 (CH^{I}CH$_3$), 26.2 (CH^{II}CH$_3$), 21.8 (CH^{I}CH_3), 18.0 (CH^{II}CH_3), 69.5 (*C*p H^{I}), 71.4 (*C*p H^{II}), 69.0 (*C*p H^{III}), 71.5 (*C*p H^{V}), 71.0 (*C*p H^{V}), 70.5 (*C*p H^{VI}), 70.0 (s, 5H, C$_5H_5^{I}$), 69.9 (s, 5H, C$_5H_5^{II}$). ^{19}F NMR ($CDCl_3$, 294 K): δ −62.13 (s), −62.22 (s), −62.25 (s), −62.30 (s). Anal. Calcd for $C_{58}H_{51}F_{12}Fe_2P_3$: C, 59.01; H, 4.35. Found: C, 59.12; H, 4.33.

Bis{(*S*)-1-[(*R*)-2-{bis[3,5-bis(trifluoromethyl)phenyl]-phosphino}ferrocenyl]ethyl}cyclohexylphosphine ((*S*)-(*R*)-8-CF$_3$-Pigiphos, 11). Cyclohexylphosphine (540 μL, 4.10 mmol) was added to a solution of (*S*)-(*R*)-4-CF$_3$-PPFA (5.47 g, 7.67 mmol) in acetic acid (25 mL), and the mixture was stirred at 76 °C for 75 h. After the solvent was evaporated at 75 °C under reduced pressure, the brown residue obtained was dissolved in *n*-hexane and was chromatographed over silica using *n*-hexane−diethyl ether (10:1) as eluent (R_f 0.64). The product obtained was dissolved in *n*-hexane and purified by short-column chromatography over silica using *n*-hexane as eluent (R_f 0.07). Pure **11** (1.70 g, 30% yield) was obtained as an orange solid. $[\alpha]^{25}_D = +221.6$. ^{1}H NMR ($CDCl_3$, 294 K): δ 3.12 (qt, 1H, CH^{I}CH$_3$, $J_{HH} = 7.2$ Hz, $J_{HP} = J_{HP} = 2.2$ Hz), 2.81 (qt, 1H, CH^{II}CH$_3$, $J_{HH} = 6.8$ Hz, $J_{HP} = J_{HP} = 3.0$ Hz), 1.53 (t, 3H, CH′CH_3), 1.47 (t, 3H, CH^{II}CH_3), 4.41 (t, 1H, Cp H^{I}), 4.33 (m, 1H, Cp H^{II}), 4.31 (t, 1H, Cp H^{III}), 4.02 (m, 1H, Cp H^{IV}), 3.92 (m, 1H, Cp H^{V}), 3.88 (m, 1H, Cp H^{VI}), 3.89 (s, 5H, C$_5H_5^{I}$), 3.87 (s, 5H, C$_5H_5^{II}$). ^{13}C NMR ($CDCl_3$, 294 K): δ 26.2 (CH^{I}CH$_3$), 24.8 (CH^{II}CH$_3$), 18.2 (CH^{I}CH_3), 20.2 (CH^{II}CH_3), 70.0 (*C*p H^{I}), 71.8 (*C*p H^{II}), 69.5 (*C*p H^{III}), 71.6 (*C*p H^{V}), 70.1 (*C*p H^{V}), 69.8 (*C*p H^{VI}), 69.9 (s, 5H, C$_5H_5^{I}$), 69.7 (s, 5H, C$_5H_5^{II}$). ^{19}F NMR ($CDCl_3$, 294 K): δ −62.03 (s), −62.12 (s), −62.14 (s), −62.21 (s). Anal. Calcd for $C_{62}H_{47}F_{24}Fe_2P_3$: C, 51.26; H, 3.26. Found: C, 51.13; H, 3.22.

Bis{(*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]-ethyl} Sulfide [(*S*)-(*R*)-*S*-Pigiphos, 12). (a) A mixture of (*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl acetate (**6**; 0.16 g, 0.35 mmol) and (*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl mercaptan (**7**; 0.15 g, 0.35 mmol) in acetic acid (15 mL) was stirred at 65 °C for 2.5 h. The solvent was removed at 65 °C in vacuo, and the residue was chromatographed over silica using *n*-hexane−EtOAc (3:1) as eluent (R_f 0.65). Crystallization of the crude product from CH_2Cl_2/MeOH gave pure **12** in 32% yield.

(b) (*S*)-1-[(*R*)-2-(Diphenylphosphino)ferrocenyl]ethyl mercaptan (**7**; 0.40 g, 0.92 mmol) in THF (10 mL) was added to a suspension of NaH (0.04 g, 0.96 mmol, 60% dispersion in mineral oil) in THF (10 mL). The resulting mixture was stirred at room temperature for 10 min. Afterward, the solvent was removed in vacuo to give an orange residue, which was dissolved in dry methanol (20 mL). To this solution was added solid (*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl acetate (**6**; 0.42 g, 0.92 mmol), and the resulting mixture was refluxed with stirring for 3 h. When the mixture cooled to room temperature, an orange solid precipitated, which was filtered off and crystallized from diethyl ether/methanol to give yellow needles of **12** in 51% yield. $[\alpha]^{25}_D = +210.0$. ^{1}H NMR ($CDCl_3$, 294 K): δ 4.11 (qd, 2H, CHCH$_3$, $J_{HH} = 6.8$ Hz, $J_{HP} = 4.1$ Hz), 1.53 (d, 6H, CHCH_3), 4.28 (t, 2H, Cp H^{I}), 4.13 (m, 2H, Cp H^{II}), 3.88 (m, 2H, Cp H^{III}), 3.96 (s, 10H, C$_5H_5$). ^{13}C NMR ($CDCl_3$, 294 K): δ 38.3 (*C*HCH$_3$), 22.9 (CH*C*H$_3$), 69.6 (*C*p H^{I}), 69.0 (*C*p H^{II}), 71.5 (*C*p H^{III}), 70.0 (s, 5H, C$_5H_5$). Anal. Calcd for $C_{48}H_{44}Fe_2P_2S$: C, 69.75; H, 5.37; S, 3.88. Found: C, 69.48; H, 5.69; S, 3.91.

Reaction of (*R*)-(*S*)-CyPFA with Cyclohexylphosphine. Cyclohexylphosphine (160 μL, 1.18 mmol) was added to a solution of (*R*)-(*S*)-CyPFA (1.07 g, 2.36 mmol) in acetic acid (15 mL), and the mixture was stirred at 75 °C for 27 h. The solvent was evaporated at 80 °C in vacuo, and the residue was chromatographed over silica using *n*-hexane−EtOAc (3:1) as eluent (R_f 0.82). Further chromatography over silica using *n*-hexane−EtOAc (33:1) as eluent (R_f 0.52) yielded a diastereomeric (1:1) mixture of (R_P and S_P)-(*R*)-{1-[(*S*)-2-(dicyclohexylphosphino)ferrocenyl]ethyl}cyclohexylphosphine (**13**) as an orange oil (25% yield). Anal. Calcd for $C_{30}H_{46}FeP_2$: C, 68.70; H, 8.84. Found: C, 68.93; H, 8.75. ^{31}P{^{1}H} NMR, diastereomer A ($CDCl_3$, 294 K): δ −13.65 (d, 1P, Cy_2P, $J_{PP} = 6.1$ Hz), −15.86 (d, 1P, CyPH, $^1J_{HP} = 213.4$ Hz from ^{31}P NMR). ^{1}H NMR, diastereomer A ($CDCl_3$, 294 K): δ 3.21 (qt, 1H, CHCH$_3$), 1.72 (t, 3H, CH_3), 3.04 (m, 1H, PH). ^{31}P{^{1}H} NMR, diastereomer B ($CDCl_3$, 294 K): δ −14.24 (br s, 1P, Cy_2P), −22.01 (br s, 1P, CyPH, $^1J_{HP} = 207.4$ Hz from ^{31}P NMR). ^{1}H NMR, diastereomer B ($CDCl_3$, 294 K): δ 2.92 (qt, 1H, CHCH$_3$), 1.58 (ddd, 3H, CH_3), 2.94 (ddd, 1H, PH).

Synthesis of the Ruthenium Complexes. [(*S*)-(*R*)-Pigiphos]RuCl$_2$ (14). (a) Solid $RuCl_2(PPh_3)_3$ (0.42 g, 0.44 mmol) was added to a solution of **8** (0.40 g, 0.44 mmol) in toluene (10 mL), and the suspension was refluxed with stirring for 4 h. During this time, a red solution was obtained, from which slowly separated out red microcrystals. After the mixture was cooled to room temperature, the solid obtained was filtered off and washed with *n*-pentane (25 mL). Yield: 87%. ^{1}H NMR (CD_2Cl_2, 294 K): δ 5.72 (b, 1H, CH^{I}CH$_3$), 3.00 (qnt, 1H, CH^{II}CH$_3$, $J_{HH} = J_{HP} = 7.6$ Hz), 1.95 (dd, 3H, CH^{I}CH_3, $J_{HH} = 7.4$, $J_{HP} = 11.1$ Hz), 1.69 (dd, 3H, CH^{II}CH_3, $J_{HP} = 10.8$ Hz), 4.73 (s, 1H, Cp H^{I}), 4.52 (s, 1H, Cp H^{II}), 4.27 (m, 2H, Cp H^{III} + Cp H^{IV}), 4.06 (s, 1H, Cp H^{V}), 3.91 (s, 1H, Cp H^{VI}), 3.86 (s, 5H, C$_5H_5^{I}$), 3.71 (s, 5H, C$_5H_5^{II}$). Anal. Calcd for $C_{54}H_{55}Cl_2Fe_2P_3Ru$: C, 60.02; H, 5.13. Found: C, 60.13; H, 5.14.

(b) A suspension of **8** (0.12 g, 0.13 mmol) and $RuCl_2(DMSO)_4$ (0.06 g, 0.13 mmol) in ethanol (15 mL) was refluxed with stirring for 2 h. A red solution was obtained, from which slowly separated out red microcrystals. After the mixture was cooled to room temperature, the solid compound was filtered off and washed with diethyl ether. Yield: 29%. Well-shaped single crystals were obtained as the bis(dichloromethane) solvate [(*S*)-(*R*)-Pigiphos]RuCl$_2$·2CH$_2$Cl$_2$ by recrystallization from CH_2Cl_2/EtOH. Anal. Calcd for $C_{56}H_{59}Cl_6Fe_2P_3Ru$: C, 53.79; H, 4.76. Found: C, 53.74; H, 4.80.

[(*R*)-(*S*)-8-Me-Pigiphos]RuCl$_2$ (15). Solid $RuCl_2(PPh_3)_3$ (0.14 g, 0.15 mmol) was added to a solution of **9** (0.15 g, 0.15 mmol) in toluene (9 mL). The mixture was refluxed with stirring for 4 h to give a deep red solution. After the mixture was cooled to room temperature, the solution was concentrated in vacuo to ca. 1 mL and *n*-pentane (10 mL) was added, causing the separation of a red oil. This was collected and dissolved in cold methanol (30 mL). The resulting solution was filtered and then evaporated to dryness in vacuo to give a red solid. Yield: 57%. ^{1}H NMR (CD_2Cl_2, 233 K): δ 3.94 (qnt, 1H, C*H*^{I}CH$_3$, $J_{HH} = J_{HP} = 7.4$ Hz), 3.00 (qnt, 1H, C*H*^{II}CH$_3$, $J_{HH} = J_{HP} = 7.3$ Hz), 2.18 (dd, 3H, CH^{I}C*H*$_3$), 1.82 (bdd, 3H, CH^{II}C*H*$_3$, $J_{HP} = 14.7$ Hz), 4.73 (bs, 1H, Cp *H*^{I}), 4.51 (bs, 1H, Cp*H*^{II}), 4.28 (m, 2H, Cp *H*^{III} + Cp *H*^{IV}), 4.51 (bs, 1H, Cp *H*^{V}), 4.50 (bs, 1H, Cp *H*^{VI}), 3.78 (s, 5H, $C_5H_5^{I}$), 3.66 (s, 5H, $C_5H_5^{II}$), 2.29 (s, 6H, Ph C*H*$_3$), 2.23 (s, 12H, Ph C*H*$_3$), 2.11 (s, 6H, Ph C*H*$_3$). Anal. Calcd for $C_{62}H_{71}Cl_2Fe_2P_3Ru$: C, 62.43; H, 6.00. Found: C, 62.56; H, 6.08.

[(*R*)-(*S*)-4-CF$_3$-Pigiphos]RuCl$_2$ (16). Solid $RuCl_2(PPh_3)_3$ (0.16 g, 0.17 mmol) was added to a solution of **10** (0.20 g, 0.17 mmol) in toluene (7 mL), and the mixture was refluxed with stirring for 5 h to give a purple-red solution. After the mixture was cooled to room temperature, the solution was concentrated in vacuo to ca. 1 mL and cold *n*-pentane (10 mL) was added, causing the separation of a red solid. Yield: 63%. ^{1}H NMR (CD_2Cl_2, 294 K): δ 3.7 (1H, C*H*^{I}CH$_3$), 2.78 (qnt, 1H, C*H*^{II}CH$_3$, $J_{HH} = J_{HP} = 7.3$ Hz), 1.95 (dd, 3H, CH^{I}C*H*$_3$, $J_{HH} = 7.0$, $J_{HP} = 10.7$ Hz), 1.80 (dd, 3H, CH^{II}C*H*$_3$, $J_{HP} = 10.0$ Hz), 4.68 (m, 2H, Cp *H*^{I} + Cp *H*^{II}), 4.43 (t, 1H, Cp *H*^{III}), 4.20 (m, 1H, Cp *H*^{IV}), 3.85 (m, 1H, Cp *H*^{V}), 3.72 (bs, 1H, Cp *H*^{VI}), 3.92 (s, 5H, $C_5H_5^{I}$), 3.81 (s, 5H, $C_5H_5^{II}$). Anal. Calcd for $C_{58}H_{51}Cl_2F_{12}Fe_2P_3Ru$: C, 51.50; H, 3.80. Found: C, 51.35; H, 3.79.

[(*S*)-(*R*)-8-CF$_3$-Pigiphos]RuCl$_2$ (17). Solid $RuCl_2(PPh_3)_3$ (0.18 g, 0.19 mmol) was added to a solution of **11** (0.27 g, 0.19 mmol) in toluene (7 mL), and the mixture was refluxed with stirring for 5 h. During this time, a purple-red solution was obtained, from which slowly separated out red microcrystals. After it was cooled to room temperature, the mixture was concentrated in vacuo to ca. 1 mL and cold *n*-pentane (25 mL) was added, causing the separation of a red solid. Yield: 72%. ^{1}H NMR (CD_2Cl_2, 223 K): δ 4.52 (qnt, 1H, C*H*^{I}CH$_3$, $J_{HH} = J_{HP} = 10.2$ Hz), 3.14 (qnt, 1H, C*H*^{II}CH$_3$, $J_{HH} = J_{HP} = 8.5$ Hz), 1.79 (m, 6H, CH^{I}C*H*$_3$ + CH^{II}C*H*$_3$), 4.37 (m, 1H, Cp *H*^{I}), 4.32 (s, 1H, Cp *H*^{II}), 3.91 (s, 1H, Cp *H*^{III}), 3.89 (s, 1H, Cp *H*^{IV}), 3.63 (s, 1H, Cp *H*^{V}), 3.24 (m, 1H, Cp *H*^{VI}), 4.14 (s, 5H, $C_5H_5^{I}$), 3.81 (s, 5H, $C_5H_5^{II}$). Anal. Calcd for $C_{62}H_{47}Cl_2F_{24}Fe_2P_3Ru$: C, 45.84; H, 2.92. Found: C, 45.79; H, 2.87.

[(*S*)-(*R*)-S-Pigiphos]RuCl$_2$ (18). Solid $RuCl_2(PPh_3)_3$ (0.16 g, 0.17 mmol) was added to a solution of **12** (0.14 g, 0.17 mmol) in toluene (8 mL), and the suspension was refluxed with stirring for 4 h. During this time, a red solution was obtained, from which slowly separated out orange microcrystals. After the mixture was cooled to room temperature, the solid obtained was filtered and washed with *n*-pentane (25 mL). Yield: 78%. ^{1}H NMR (CD_2Cl_2, 294 K): δ 3.36 (q, 1H, C*H*^{I}CH$_3$, $J_{HH} = 7.4$ Hz), 2.76 (1H, C*H*^{II}CH$_3$), 1.75 (d, 3H, CH^{I}C*H*$_3$), 1.87 (d, 3H, CH^{II}C*H*$_3$, $J_{HH} = 6.1$ Hz), 4.46 (m, 2H, Cp *H*^{I} + Cp *H*^{II}), 4.35 (m, 1H, Cp *H*^{III}), 3.87 (s, 1H, Cp *H*^{IV}), 3.76 (m, 1H, Cp *H*^{V}), 2.76 (s, 1H, Cp *H*^{VI}), 4.20 (s, 5H, $C_5H_5^{I}$), 4.14 (s, 5H, $C_5H_5^{II}$). Anal. Calcd for $C_{48}H_{44}Cl_2Fe_2P_2RuS$: C, 57.74; H, 4.44. Found: C, 57.59; H, 4.41.

{***mer*-[(*S*)-(*R*)-Pigiphos]Ru(CH$_3$CN)$_3$}(BF$_4$)$_2$ (19).** Solid $[Ru(NBD)(CH_3CN)_4](BF_4)_2$ (0.11 g, 0.21 mmol) was added to an orange solution of **8** (0.19 g, 0.21 mmol) in toluene (7 mL). The suspension was refluxed with stirring for 18 h to give a yellow solution, from which slowly separated out a yellow-ocher solid. After the mixture was cooled to room temperature, *n*-pentane (10 mL) was added and the solid compound was filtered off and then washed with *n*-pentane. Crystallization from acetonitrile−diethyl ether gave **19** in 38% yield. ^{1}H NMR (CD_2Cl_2, 294 K): δ 3.46 (qnt, 1H, C*H*^{I}CH$_3$, $J_{HH} = J_{HP} = 7.1$ Hz), 3.04 (qnt, 1H, C*H*^{II}CH$_3$, $J_{HH} = J_{HP} = 7.9$ Hz), 2.05 (dd, 3H, CH^{I}C*H*$_3$, $J_{HP} = 10.2$ Hz), 1.81 (dd, 3H, CH^{II}C*H*$_3$, $J_{HP} = 11.9$ Hz), 4.73 (m, 1H, Cp *H*^{I}), 4.69 (m, 1H, Cp *H*^{II}), 4.52 (m, 1H, Cp *H*^{III}), 4.49 (m, 1H, Cp *H*^{IV}), 4.45 (m, 1H, Cp *H*^{V}), 3.35 (m, 1H, Cp *H*^{VI}), 4.36 (s, 5H, $C_5H_5^{I}$), 3.55 (s, 5H, $C_5H_5^{II}$). Anal. Calcd for $C_{60}H_{64}N_3B_2F_8Fe_2P_3Ru$: C, 55.16; H, 4.94; N, 3.22. Found: C, 55.28; N, 4.92; N, 3.38. IR: 2341, 2333, 2298 ν(C−N) cm^{-1}.

{**[(*S*)-(*R*)-Pigiphos]RuCl(CH$_3$CN)$_2$}PF$_6$ (20).** Solid $TlPF_6$ (0.02 g, 0.06 mmol) was added to a solution of **14** (0.07 g, 0.06 mmol) in CH_3CN (3 mL). After it was stirred for 15 min, the mixture was decanted and TlCl was filtered off. By addition of diethyl ether (20 mL) an orange oil which solidified on standing separated out. The solid compound was filtered and recrystallized from acetonitrile−diethyl ether to give pure **20** in 33% yield. ^{1}H NMR (CD_2Cl_2, 243 K): δ 3.70 (bs, 1H, C*H*^{I}CH$_3$), 3.29 (bs, 1H, C*H*^{II}CH$_3$), 1.80 (b, 6H, CH^{I}C*H*$_3$ + CH^{II}C*H*$_3$), 4.82 (s, 1H, Cp *H*^{I}), 4.60 (s, 1H, Cp *H*^{II}), 4.51 (s, 1H, Cp *H*^{III}), 4.40 (s, 1H, Cp *H*^{IV}), 4.05 (bs, 2H, Cp *H*^{V} + Cp *H*^{VI}), 4.22 (s, 5H, $C_5H_5^{I}$), 3.86 (s, 5H, $C_5H_5^{II}$), 1.98 (s, 3H, C*H*$_3$CN), 1.57 (s, 3H, C*H*$_3$CN). Anal. Calcd for $C_{58}H_{61}N_2ClF_6Fe_2P_4Ru$: C, 54.76; H, 4.83; N, 2.20. Found: C, 54.67; H, 4.73; N, 2.31. IR: 2353, 2319 ν(C−N) cm^{-1}.

{***fac*-[(*S*)-(*R*)-Pigiphos]Ru(CH$_3$CN)$_3$}(PF$_6$)$_2$ (21).** Solid $TlPF_6$ (0.15 g, 0.43 mmol) was added to a red-orange solution of **14** (0.23 g, 0.21 mmol) in CH_3CN (7 mL). After it was stirred for 15 min, the mixture was decanted and TlCl was filtered off. By addition of diethyl ether (20 mL) to the resulting yellow-orange solution an orange solid separated out. This was filtered and washed with diethyl ether (20 mL). Yield: 68%. ^{1}H NMR (CD_2Cl_2, 294 K): δ 3.40 (qnt, 1H, C*H*^{I}CH$_3$, $J_{HH} = J_{HP} = 7.3$ Hz), 2.40 (qnt, 1H, C*H*^{II}CH$_3$, $J_{HH} = J_{HP} = 7.2$ Hz), 2.01 (dd, 3H, CH^{I}C*H*$_3$, $J_{HP} = 10.7$ Hz), 1.87 (dd, 3H, CH^{II}C*H*$_3$, $J_{HP} = 10.8$ Hz), 4.73 (bt, 1H, Cp *H*^{I}), 4.51 (bt, 1H, Cp *H*^{II}), 4.28 (m, 1H, Cp *H*^{III}), 4.19 (m, 1H, Cp *H*^{IV}), 3.57 (dt, 1H, Cp *H*^{V}), 3.51 (dt, 1H, Cp *H*^{VI}), 4.32 (s, 5H, $C_5H_5^{I}$), 3.69 (s, 5H, $C_5H_5^{II}$). Anal. Calcd for $C_{60}H_{64}N_3F_{12}Fe_2P_5Ru$: C, 50.65; H, 4.53; N, 2.95. Found: C, 50.61; H, 4.55; N, 2.73. IR: 2343, 2307, 2301 ν(C−N) cm^{-1}.

{**[(*R*)-(*S*)-8-Me-Pigiphos]Ru(CH$_3$CN)$_3$}(PF$_6$)$_2$ (22).** This compound was prepared as described above for **21** by using **15** instead of **14**. Yield: 48%. ^{1}H NMR (CD_2Cl_2, 294 K): δ 3.35 (qnt, 1H, C*H*^{I}CH$_3$, $J_{HH} = J_{HP} = 7.4$ Hz), 2.60 (qnt, 1H, C*H*^{II}CH$_3$, $J_{HH} = J_{HP} = 7.0$ Hz), 1.89 (t, 3H, CH^{I}C*H*$_3$), 1.87 (t, 3H, CH^{II}C*H*$_3$), 4.48 (s, 1H, Cp *H*^{I}), 4.43 (s, 1H, Cp *H*^{II}), 4.12 (s, 1H, Cp *H*^{III}), 3.65 (m, 1H, Cp *H*^{IV}), 2.97 (m, 1H, Cp *H*^{V}), 2.78 (m, 1H, Cp *H*^{VI}), 4.16 (s, 5H, $C_5H_5^{I}$), 4.01 (s, 5H, $C_5H_5^{II}$), 2.38 (s, 12H, Ph C*H*$_3$), 2.2 (bs, 6H, Ph C*H*$_3$), 2.0 (bs, 6H, Ph C*H*$_3$). Anal. Calcd for $C_{68}H_{80}N_3F_{12}Fe_2P_5Ru$: C, 53.21; H, 5.25; N, 2.74. Found: C, 53.32; H, 5.16; N, 2.69. IR: 2320, 2312, 2290 ν(C−N) cm^{-1}.

{**[(*R*)-(*S*)-4-CF$_3$-Pigiphos]Ru(CH$_3$CN)$_3$}(PF$_6$)$_2$ (23).** This compound was prepared as described above for **21** by using **16** instead of **14**. Yield: 65%. ^{1}H NMR (CD_2Cl_2, 294 K): δ 3.25 (qnt, 1H, C*H*^{I}CH$_3$, $J_{HH} = J_{HP} = 7.1$ Hz), 2.69 (bqnt, 1H, C*H*^{II}CH$_3$, $J_{HH} = J_{HP} = 6.9$ Hz), 1.95 (dd, 3H, CH^{I}C*H*$_3$, $J_{HP} = 11.0$ Hz), 1.94 (dd, 3H, CH^{II}C*H*$_3$, $J_{HP} = 12.9$ Hz), 4.73 (s, 1H, Cp *H*^{I}), 4.61 (t, 1H, Cp *H*^{II}), 4.23 (s, 1H, Cp *H*^{III}), 4.04 (1H, Cp *H*^{IV}), 2.82 (m, 2H, Cp *H*^{V} + Cp *H*^{VI}), 4.22 (s, 5H, $C_5H_5^{I}$), 4.04 (s, 5H, $C_5H_5^{II}$). Anal. Calcd for $C_{64}H_{60}N_3F_{24}Fe_2P_5Ru$: C, 45.36; H, 3.57; N, 2.48. Found: C, 45.46; H, 3.61; N, 2.54. IR: 2344, 2328, 2300 ν(C−N) cm^{-1}.

{**[(*S*)-(*R*)-8-CF$_3$-Pigiphos]RuCl(CH$_3$CN)$_2$}PF$_6$ (24).** This compound was prepared as described above for **21** by using **17** instead of **14**. Yield: 76%. ^{1}H NMR (CD_2Cl_2, 294 K): δ 3.13 (qnt, 1H, C*H*^{I}CH$_3$, $J_{HH} = J_{HP} = 6.9$ Hz), 2.47 (qnt, 1H, C*H*^{II}CH$_3$, $J_{HH} = J_{HP} = 6.7$ Hz), 1.90 (dd, 3H, CH^{I}C*H*$_3$, $J_{HP} = 10.1$ Hz), 1.92 (dd, 3H, CH^{II}C*H*$_3$, $J_{HP} = 9.9$ Hz), 4.70 (s, 1H, Cp *H*^{I}), 4.53 (s, 1H, Cp *H*^{II}), 4.36 (s, 1H, Cp *H*^{III}), 3.68 (s, 1H, Cp *H*^{IV}), 2.77 (s, 1H, Cp *H*^{V}), 2.51 (s, 1H, Cp *H*^{VI}), 4.20 (s, 5H, $C_5H_5^{I}$), 4.05 (s, 5H, $C_5H_5^{II}$). Anal. Calcd for $C_{66}H_{53}N_2ClF_{30}Fe_2P_4Ru$: C, 43.65; H, 2.94; N, 1.54. Found: C, 43.52; H, 2.89; N, 1.53. IR: 2316, 2299, 2286 ν(C−N) cm^{-1}.

{**[(*S*)-(*R*)-S-Pigiphos]Ru(CH$_3$CN)$_3$}(PF$_6$)$_2$ (25).** This compound was prepared as described above for **21** by using **18** instead of **14**. Yield: 65%. ^{1}H NMR (acetone-d_6, 294 K): δ 4.26 (q, 1H, CH^{I}CH$_3$, J_{HH} = 7.4 Hz), 2.92 (q, 1H, CH^{II}CH$_3$, J_{HH} = 6.3 Hz), 2.45 (d, 3H, CH^{I}CH_3), 1.98 (d, 3H, CH^{II}CH_3), 5.20 (m, 1H, Cp H^{I}), 4.93 (t, 1H, Cp H^{II}), 4.76 (m, 1H, Cp H^{III}), 4.64 (m, 1H, Cp H^{IV}), 4.48 (m, 1H, Cp H^{V}), 4.37 (m, 1H, Cp H^{VI}), 4.43 (s, 5H, C$_5H_5^{I}$), 3.52 (s, 5H, C$_5H_5^{II}$). Anal. Calcd for C$_{54}$H$_{53}$N$_3$F$_{12}$Fe$_2$P$_4$RuS: C, 48.38; H, 3.98; N, 3.13. Found: C, 48.31; H, 4.01; N, 3.09. IR: 2330, 2314, 2311 ν(C−N) cm^{-1}.

[(*S*)-(*R*)-Pigiphos]Ru(CF$_3$CO$_2$)$_2$ (26). Solid [Ru$_2$(CF$_3$CO$_2$)$_4$-(COD)$_2$H$_2$O] (0.10 g, 0.11 mmol) was added to a solution of **8** (0.20 g, 0.22 mmol) in toluene (10 mL), and the mixture was refluxed with stirring for 36 h. A red solution was obtained, which was cooled to room temperature and filtered. The addition of *n*-hexane (10 mL) to the filtrate led to the precipitation of a yellow-ocher solid. This was decanted, washed with *n*-hexane, and dried in vacuo. Recrystallization from THF/*n*-hexane gave pure **26** in 56% yield. ^{1}H NMR (THF-d_8, 253 K): δ 5.61 (dq, 1H, CH^{I}CH$_3$, J_{HH} = 7.3, J_{HP} = 14.8 Hz), 4.1 (1H, CH^{II}CH$_3$), 1.96 (dd, 3H, CH^{I}CH_3, J_{HP} = 10.8 Hz), 2.12 (dd, 3H, CH^{II}CH_3, J_{HH} = 7.3, J_{HP} = 11.4 Hz), 4.96 (s, 1H, Cp H^{I}), 4.91 (s, 1H, Cp H^{II}), 4.46 (m, 2H, Cp H^{III} + Cp H^{IV}), 4.18 (s, 1H, Cp H^{V}), 3.82 (s, 1H, Cp H^{VI}), 4.08 (s, 5H, C$_5H_5^{I}$), 3.91 (s, 5H, C$_5H_5^{II}$). Anal. Calcd for C$_{58}$H$_{55}$F$_6$Fe$_2$O$_4$P$_3$Ru: C, 56.37; H, 4.49. Found: C, 56.44; H, 4.51.

X-ray Crystal Structure Determination of 14·2CH$_2$Cl$_2$. X-ray data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with a graphite-oriented monochromator utilizing Mo Kα radiation (λ = 0.710 69 Å). The final unit cell parameters were obtained by least-squares refinement of the setting angles of 25 reflections that had been accurately centered on the diffractometer. The intensities of two standard reflections were measured every 120 min of X-ray exposure. No decay was observed. The structure was solved by direct methods using the SIR92 program, and all of the non-hydrogen atoms were found through a series of F_o Fourier maps. Hydrogen atoms were introduced at calculated positions. The refinement was done by full-matrix least-squares calculations, initially with isotropic thermal parameters. The refinement, for 629 parameters and 3845 reflections with $I > 2\sigma(I)$, converted to $R = 0.0754$ ($R_w^2 = 0.3950$ for all 5206 data). The absolute configuration was confirmed by the refinement of the Flack parameter. Models reached convergence with $R = \sum(||F_o| - |F_c||)/\sum(|F_o|)$ and $R_w^2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$. The calculations were carried out by using the SHELX93 and ORTEP[19] programs. Details of data collection and refinement are given in Table 1.

General Procedure for the Reduction of Acetophenone *via* Hydrogen Transfer. In a typical reaction, a catalyst precursor (0.002 mmol) and freshly distilled acetophenone (26 μL, 0.2 mmol) were introduced under Ar into a flask equipped with a condenser and containing 5 mL of anhydrous *i*-PrOH. The mixture was heated to 68 °C with stirring. After 5 min, freshly prepared *i*-PrOK (0.1 M in *i*-PrOH, 22 μL, 0.002 mmol) was introduced. The addition of *i*-PrOK was considered as the starting time of the reaction. The solution was stirred at 68 °C for 2 h. During this time the reaction evolution was monitored by GC (SPB-1 capillary column). After the reaction was quenched by cooling down to room temperature, the solvent was removed in vacuo. The residue was dissolved in 1 mL of diethyl ether and chromatographed by short-column chromatography over silica using diethyl ether as eluent. The enantiomeric excess was determined on the resulting solution by GC analysis (Chiraldex G-TA capillary column) using He as the carrier gas (flow 1.0 mL/min) and isothermal conditions (90 °C). Retention times are 15.9 and 16.8 min for the *R* and *S* enantiomers of 1-phenylethanol, respectively.

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Table 1. Summary of Crystallographic Data for [(*S*)-(*R*)-Pigiphos]RuCl$_2$·2CH$_2$Cl$_2$

empirical formula	C$_{56}$H$_{59}$Cl$_6$Fe$_2$P$_3$Ru
fw	1250.41
temp, K	293
wavelength, Å	0.71069
cryst syst	orthorhombic
space group	$P2_12_12_1$
unit cell dimens	
a, Å	11.362(2)
b, Å	13.992(2)
c, Å	33.523(4)
α, deg	90.0
β, deg	90.0
γ, deg	90.0
V, Å^3	5329.4(8)
Z	4
D(calcd), g/cm^3	1.558
abs coeff, mm^{-1}	1.246
θ range for data collcn, deg	2.56−24.96
index ranges	$0 \le h \le 13$, $0 \le k \le 16$, $0 \le l \le 39$
no. of collcd rflns	5206
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	5094/0/629
goodness of fit	1.040
final *R* index ($I > 2\sigma(I)$)	0.0754
R indices (all data)	$R = 0.1243$, $R_w^2 = 0.3950$
abs structure param	0.02(8)

Results and Discussion

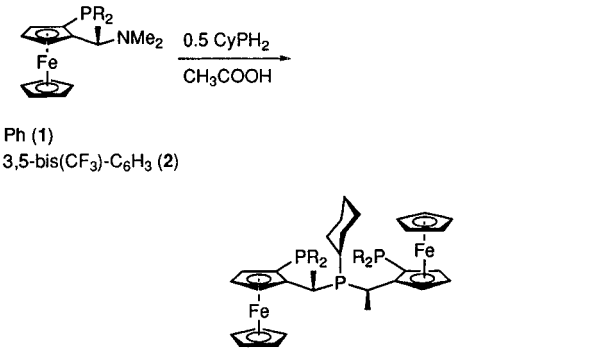
Synthesis and Characterization of the Chiral Bis(ferrocenyl)−Triphosphine Ligands. All the chiral tridentate phosphine ligands **8**−**11** illustrated in Scheme 1 have been prepared in satisfactory yields by the reaction of cyclohexylphosphine with a 2-fold excess of the corresponding chiral ferrocenyl aminophosphine **1**, **2**, **4**, or **5** in hot acetic acid (Scheme 1).

The electron-withdrawing character of the phosphorus substituents determines the reactivity of the ferrocenyl amino compounds, which decreases in the order 3,5-(CH$_3$)$_2$-Ph > Ph > 3-CF$_3$-Ph > 3,5-(CF$_3$)$_2$-Ph. As an example, the optimized reaction conditions for the reaction of (*S*)-(*R*)-PPFA (**1**) and (*S*)-(*R*)-4-CF$_3$-PPFA (**2**) with cyclohexylphosphine are 7 h at 65 °C and 75 h at 76 °C, respectively. During all reactions, the formation of variable amounts (5−15%) of the elimination product 1-(diarylphosphino)-2-vinylferrocene are formed. Nevertheless, a satisfactory purification can be achieved by either column chromatography or recrystallization. The vinylferrocene side product and other unidentified compounds are exclusively obtained when either phenylphosphine or cyclohexylamine replaces cyclohexylphosphine in the reaction with the ferrocenyl aminophosphines. This result suggests that cyclohexylphosphine possesses the appropriate balance of nucleophilicity and basicity to favor the coupling of the two ferrocenyl units over dimethylamine elimination.

The sulfur-bridged bis(ferrocenyl) ligand (*S*)-(*R*)-S-Pigiphos (**12**) has been synthesized by the substitution reaction of (*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]-ethyl acetate (**6**) with either (*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl mercaptan (**7**) in hot acetic acid or (*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl mercaptan sodium salt in dry methanol (Scheme 1). All the above reactions proceed with retention of configuration on the side-chain stereocenters.

The reaction of (*R*)-(*S*)-CyPFA (**3**) with $^1/_2$ equiv of cyclohexylphosphine in acetic acid at 75 °C for 27 h produces a ca. 1:1 diastereomeric mixture of (R_P)-(*R*)-

Scheme 1

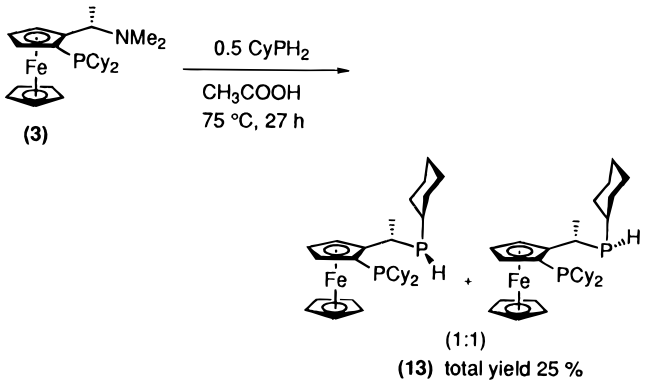


and(S_P)-(R)-{1-[(S)-2-(dicyclohexylphosphino)ferrocenyl]-ethyl}cyclohexylphosphine (**13**) in 25% yield (Scheme 2). Analogous diastereomeric mixtures were obtained under different reaction conditions. All our attempts to separate the pairs of diastereomers by column chromatography were unsuccessful. Further reaction to afford the tridentate ligand is probably hampered by steric reasons.

$^{31}P\{^1H\}$ NMR data for the chiral ligands **8**−**12** in $CDCl_3$ solutions at 296 K are collected in Table 2. Selected ^1H and ^{13}C NMR data are reported in the Experimental Section.

In the tridentate bis(ferrocenyl) phosphines **8**−**11**, the two ferrocenyl units are diastereotopic and are consequently characterized by two distinct sets of ^{31}P, ^1H, and ^{13}C NMR resonances. As an example, the ^{31}P spectrum of (R)-(S)-8Me-Pigiphos (**9**) contains two doublets (−25.22 and −25.10 ppm) attributable to the two diarylphosphino groups (P_A and P_B, respectively) which are coupled to the central CyP phosphorus (15.33 ppm, $J_{PP_A} = 26.6$, $J_{PP_B} = 6.7$ Hz). The absence of any symmetry element relating the two ferrocenyl fragments in **9** is clearly

Scheme 2



visible from the ^1H NMR spectrum, which shows two side-chain methyl resonances ($CHCH_3^I$ and $CHCH_3^{II}$, 1.61 and 1.56 ppm, respectively), two methylene resonances ($CHCH_3^I$ and $CHCH_3^{II}$, 3.18 and 2.80 ppm, respectively), two unsubstituted cyclopentadienyl singlets (3.93 and 3.86 ppm), and four Ph−CH_3 singlets (2.41, 2.37, 2.32, and 2.27 ppm).

The only ligand in which the two ferrocenyl moieties are magnetically equivalent (due to a C_2 axis passing through the sulfur atom) is the sulfur-bridged ligand **12**. Indeed, the ^{31}P spectrum of the latter compound consists of a singlet at −23.67 ppm, while the ^1H spectrum shows resonances attributable to a unique ferrocenylphosphino group.

The ^{31}P NMR parameters of the bis(ferrocenyl)−triphosphine ligands **8**−**11** show a number of common characteristics (Table 2). The resonances of the central CyP phosphorus atoms fall at positive-field values and appear as doublets or doublets due to coupling to the two magnetically inequivalent terminal P_A and P_B nuclei. These, in turn, show negative δ values. The chemical shifts of all ^{31}P nuclei are significantly influenced by the electron-withdrawing character of the phosphine substituents; *i.e.*, they move downfield on going from (R)-(S)-8-Me-Pigiphos to (S)-(R)-8-CF_3-Pigiphos. In all ligands, the two $^4J_{PP}$ values are different from each other (by *ca.* 20 ppm), which indicates that the relative orientations of the phosphorus lone-pair vectors are different in the two ferrocenyl−phosphine moieties.[20]

The ^1H NMR spectra of the ligands **8**−**11** are similar to those reported for other mono(ferrocenyl) 1,3-bis(phosphino) ligands[21] and do not deserve any particular comment.

Synthesis and Characterization of Chiral Ruthenium Dichloride Complexes. Monomeric neutral Ru(II) complexes of the general formula (L)$RuCl_2$ (**14**−**18**) can be synthesized with all the chiral tridentate ligands described above. As starting Ru(II) compounds, either $RuCl_2(DMSO)_4$ or $RuCl_2(PPh_3)_3$ can be employed. All of the dichloride complexes are quite air-stable in both the solid state and solution with noncoordinating solvents (*i.e.* CH_2Cl_2, C_6H_6), except for the 4-CF_3-Pigiphos and 8-CF_3-Pigiphos derivatives, which are extremely air- and moisture-sensitive. The color of the complexes ranges from red for (Pigiphos)$RuCl_2$ to violet

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Table 2. $^{31}P\{^1H\}$ NMR Data for the Ligands[a]

ligand	(Cy)P	P_A	P_B
(*S*)-(*R*)-Pigiphos (**8**)[b]	15.60 (dd); $J_{PP_A} = 9.9$, $J_{PP_B} = 28.1$	−26.04 (d)	−26.04 (d)
(*R*)-(*S*)-8-Me-Pigiphos (**9**)	15.33 (dd); $J_{PP_A} = 26.6$, $J_{PP_B} = 6.7$	−25.10 (d)	−25.22 (d)
(*R*)-(*S*)-4-CF_3-Pigiphos (**10**)	17.88 (dd); $J_{PP_A} = 11.7$, $J_{PP_B} = 32.7$	−24.32 (d)	−24.80 (d)
(*S*)-(*R*)-8-CF_3-Pigiphos (**11**)	20.97 (dd); $J_{PP_A} = 12.6$, $J_{PP_B} = 35.2$	−21.16 (d)	−21.91 (d)
(*S*)-(*R*)-S-Pigiphos (**12**)		−23.67 (s) (2P)	

[a] Chemical shifts in ppm, coupling constants in Hz; 202.47 MHz, $CDCl_3$, 296 K. Abbreviations: s, singlet; d, doublet. [b] Data from ref 6.

Table 3. $^{31}P\{^1H\}$ NMR Data for the Complexes[a]

complex	(Cy)P	(Ph)P_A	(Ph)P_B
[(*S*)-(*R*)-Pigiphos]$RuCl_2$ (**14**)			
294 K	81.02 (bs)	64.66 (bs)	19.12 (bs)
243 K	79.55 (dd)	69.71 (t); $J_{PP} = 35.7$	14.52 (t); $J_{PP} = 32.1$
[(*R*)-(*S*)-8-Me-Pigiphos]$RuCl_2$ (**15**)[c]	71.92 (t); $J_{PP} = 38.6$	66.09 (t)	6.50 (t)
[(*R*)-(*S*)-4-CF_3-Pigiphos]$RuCl_2$ (**16**)[d]	81.15 (t)	50.88 (t)	34.18 (t); $J_{PP} = 36.0$
[(*S*)-(*R*)-8-CF_3-Pigiphos]$RuCl_2$ (**17**)			
294 K	102.21 (bs)	70.46 (bs)	53.4 (bs)
223 K	87.87 (dd); $J_{PP} = 27.5$, $J_{PP} = 36.3$	52.75 (dd) (2P)	
[(*S*)-(*R*)-S-Pigiphos]$RuCl_2$ (**18**)		50.31 (d); $J_{PP} = 36.8$	37.49 (d)
{*mer*-[(*S*)-(*R*)-Pigiphos]$Ru(CH_3CN)_3\}^{2+}$ (**19**)	77.04	29.40;[f] $J_{PP_A} = 23.5$, $J_{P_AP_B} = 264.5$	20.24;[f] $J_{PP_B} = 29.8$
{[(*S*)-(*R*)-Pigiphos]$RuCl(CH_3CN)_2\}^+$ (**20**)[b]	85.19 (t); $J_{PP} = 29.8$	35.42 (t)	32.18 (t)
{*fac*-[(*S*)-(*R*)-Pigiphos]$Ru(CH_3CN)_3\}^{2+}$ (**21**)	81.50 (t); $J_{PP} = 30.5$	40.55 (t)	31.22 (t)
{[(*R*)-(*S*)-8-Me-Pigiphos]$Ru(CH_3CN)_3\}^{2+}$ (**22**)	83.71 (t); $J_{PP} = 30.6$	45.47 (t)	31.31 (t)
{[(*R*)-(*S*)-4CF_3-Pigiphos]$Ru(CH_3CN)_3\}^{2+}$ (**23**)	81.92 (t); $J_{PP} = 33.3$	52.01 (t)	35.24 (t)
{[(*S*)-(*R*)-8CF_3-Pigiphos]$RuCl(CH_3CN)_2\}^+$ (**24**)	86.59 (t); $J_{PP} = 31.0$	51.67 (t)	38.71 (t)
{[(*S*)-(*R*)-S-Pigiphos]$Ru(CH_3CN)_3\}^{2+}$ (**25**)[e]		52.62 (d); $J_{PP} = 30.2$	43.56 (d)
[(*S*)-(*R*)-Pigiphos]$Ru(CF_3CO_2)_2$ (**26**)			
THF-d_8, 294 K	102.26 (bs)	47.32 (bs)	44.56 (bs)
THF-d_8, 253 K	101.30 (dd); $J_{PP_A} = 30.5$, $J_{PP_B} = 45.7$	47.01 (t); $J_{P_AP_B} = 30.5$	44.94 (dd)
CD_2Cl_2, 253 K	101.48 (t); $J_{PP} = 42.8$	46.61 (t)	44.71 (t)

[a] 202.47 MHz, 294 K, CD_2Cl_2; chemical shifts in ppm, coupling constants in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; b, broad. [b] 243 K. [c] 233 K. [d] 193 K. [e] Acetone-d_6. [f] AMN spin system. Data from computer simulation.

for (8-CF_3-Pigiphos)$RuCl_2$. The sulfur-bridged (S-Pigiphos)$RuCl_2$ complex is orange.

$^{31}P\{^1H\}$ NMR data for the complexes in CD_2Cl_2 solutions are reported in Table 3, and selected ^1H NMR data are reported in the Experimental Section. Unlike the free ligands, the tridentate phosphine complexes **14**−**17** are slightly fluxional on the NMR time scale in room-temperature solutions, where the ^{31}P NMR spectra consist of AMQ patterns with no discernible J_{PP} coupling constants. In the temperature range from 243 to 193 K, however, the slow-motion regime is attained by all compounds to give resolved patterns with J_{PP} values ranging from 27 to 38 Hz. A *fac* arrangement of all ligands about the metal center can thus be anticipated.[22,23] Stereochemical nonrigidity in solution is a typical characteristic of many five-coordinate ruthenium(II) complexes with linear tridentate phosphine ligands.[24]

Two types of ^{31}P NMR spectra are observed for the dichloride Ru complexes: (i) those in which the CyP resonances and one PhP resonance are separated from each other by *ca*. 8 ppm and by *ca*. 60 ppm from the other PhP phosphorus, which resonates at higher field (**14**, **15**) and (ii) those in which the CyP resonance is the lowest field signal, separated by *ca*. 30 ppm from the two PhP signals, which in turn are separated by *ca*. 17 ppm from each other (**16**, **17**). The central CyP resonances have been unequivocally assigned on the basis of 2D ^1H,^{31}P spectra through correlations with the methylene and methyl protons. Having established that the Ru complexes may have different structures in solution and that the bis(ferrocenyl)−triphosphine ligands do not adopt a *mer* arrangement, it remains for us to discriminate between square-pyramidal and trigonal-bipyramidal structures, though considerable distortions from the idealized geometries may be possible in either case due to the constraints imposed by the polydentate nature of the ligands. Simple *trans*-influence arguments can address this point, as previously reported for the related dichloride polyphosphine Ru complexes *fac*-(Cyttp)$RuCl_2$[24] (Cyttp = $PhP(CH_2CH_2CH_2PCy_2)_2$), (ttp*)$RuCl_2$[7d] (ttp* = $PhP(CH_2CH(CH_3)CH_2PPh_2)_2$), and $RuCl_2[P(OEt)Ph_2]_3$.[25] In particular, from a comparison with the ^{31}P NMR spectra of the free ligands (Table 2), one may distinguish the phosphorus atoms *trans* to chlorine from those with no *trans* ligand by the upfield shift of *ca*. 30 ppm of their resonance.[7d,23−30] By using this simple criterion, the Pigiphos and 8-Me-Pigiphos complexes **14** and **15** can be assigned a *fac* square-pyramidal structure with an apical PhP group (Chart 1), whereas the 4-CF_3-Pigiphos and 8-CF_3-Pigiphos complexes **16** and **17** are assigned a *fac* trigonal-

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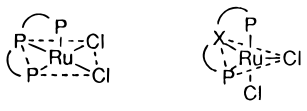
Chart 1



14, 15 **16-18**

X = P, S

bipyramidal structure with one chloride and one terminal phosphorus atom occupying the axial positions.

Interestingly, complex **17** is thermochromic in CH_2Cl_2 solutions, being red at room temperature and yellow at $T \leq 223$ K. As shown by variable-temperature ^{31}P NMR spectroscopy (Table 3), the color change is accompanied by a structural change of the complex. At 223 K, the central phosphorus atom resonance is shifted upfield by *ca.* 14 ppm as compared to the room-temperature spectrum, while the two terminal phosphorus atoms become isochronous and resonate at nearly the same frequency (53 ppm) observed for the phosphorus atom *trans* to chlorine in the square-pyramidal complexes. On the basis of the *trans*-influence criterion discussed above, the low-temperature behavior of **17** may be interpreted by the formation of a six-coordinate species, either a μ-Cl_3 dimer, analogous to $[Ru_2(\mu\text{-}Cl)_3(L)_2]Cl$ (L = CF_3PPP,[31] ETP,[32] triphos,[33] PNP[34]), or a μ-Cl_2 dimer, analogous to $[Ru_2Cl_2(\mu\text{-}Cl)_2(TTP)_2]$.[35] Variable-temperature conductivity measurements have addressed this point, showing that the molar conductance increases as the temperature decreases (from 0.2 Ω^{-1} cm^2 mol^{-1} for **17** in CH_2Cl_2 at room temperature to 62 Ω^{-1} cm^2 mol^{-1} at 220 K). Accordingly, a cationic μ-Cl_3 structure is assigned to **17** at low temperatures.[32]

The ^{31}P NMR spectrum of the S-Pigiphos dichloride complex **18** consists of two doublets separated by ca. 13 ppm with a J_{PP} coupling constant of 36.8 Hz that is typical for a *cis* arrangement of the terminal phosphorus.[22,23] Since the complex is stereochemically rigid on the NMR time scale in room-temperature solutions, its ^{31}P NMR parameters suggest that this compound assumes a *fac* trigonal-bipyramidal structure as reported above for **16** and **17**.

In CD_3CN solution, the ^{31}P NMR spectra of the dichloride complexes are dramatically different from those recorded in CD_2Cl_2,[36] most likely due to the formation of acetonitrile adducts (see below). Despite the coordinative unsaturation of the dichloride complexes, however, no MeCN adduct can be isolated by recrystallization of **14**−**18** from MeCN.

Solid-State Structure of 14·2CH_2CL_2. A single-crystal X-ray analysis of **14**·2CH_2Cl_2 has confirmed the structural assignment proposed on the basis of the NMR parameters. Selected bond distances and angles are reported in Table 4, and an ORTEP view of the complex molecule is shown in Figure 1.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [(*S*)-(*R*)-Pigiphos]$RuCl_2$·2CH_2Cl_2

Ru−P(1)	2.294(4)	Ru−Cl(1)	2.425(5)
Ru−P(2)	2.231(5)	Ru−Cl(2)	2.447(5)
Ru−P(3)	2.291(4)		
P(2)−Ru−P(3)	88.2(2)	P(2)−Ru−Cl(2)	106.0(2)
P(2)−Ru−P(1)	101.9(2)	P(3)−Ru−Cl(2)	165.0(2)
P(3)−Ru−P(1)	91.8(2)	P(1)−Ru−Cl(2)	89.7(2)
P(3)−Ru−Cl(1)	90.3(2)	Cl(1)−Ru−Cl(2)	82.9(2)
P(1)−Ru−Cl(1)	158.1(2)	P(2)−Ru−Cl(1)	99.9(2)

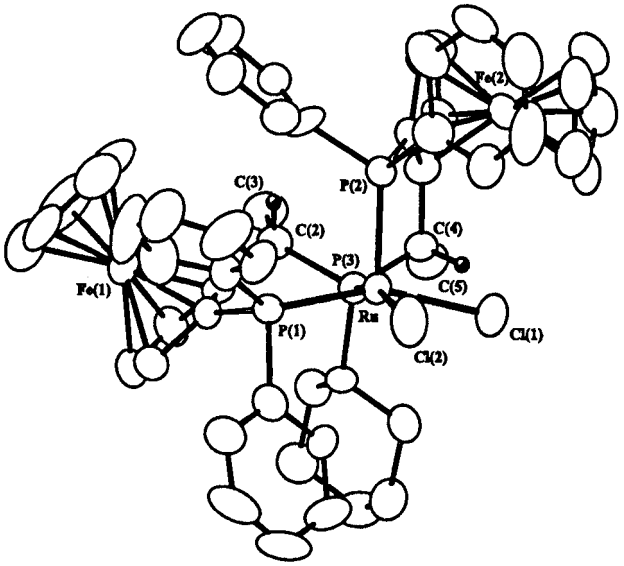


Figure 1. ORTEP drawing of the complex [(*S*)-(*R*)-Pigiphos]-$RuCl_2$·2CH_2Cl_2 (**14**·2CH_2Cl_2). Dichloromethane molecules are omitted for clarity.

The coordination geometry around the metal center approximates a square pyramid in which the (Ph)P(2) atom occupies the apical position and the Cl(1) and Cl(2) atoms are *trans* to (Ph)P(1) and (Cy)P(3), respectively. The main distortions from the idealized geometry are shown by the P(1)−Ru−Cl(1) (158.1(2)°) and P(3)−Ru−Cl(2) (165.0(2)°) angles as well as the displacement (0.36 Å) of the Ru atom above the best plane comprising the basal donor atoms (P(1), P(3), Cl(1), and Cl(2); maximum deviations ±0.07 Å). Nevertheless, considering the best idealized coordination plane of Ru (deviations are 0.29 Å for Ru and +0.01 to −0.14 Å for the four basal donors), one may notice that (i) the cyclohexyl ring lies below this plane (distance of the ipso carbon C(51) from the plane −1.82 Å) and assumes a pseudoaxial arrangement (P(1)−Ru−P(3)−C(51) = 76.86°) with respect to this plane, (ii) the two side-chain methyne carbons, one methyl group, and one ferrocenyl unit lie above the plane (distances: C(2), 0.72 Å; C(4), 0.74 Å; C(3), 1.12 Å; Fe(2), 3.49 Å), and (iii) the other methyl and ferrocenyl groups are almost in plane (distances: C(5), 0.29 Å; Fe(1), 0.22 Å). From a side view of the complex (Figure 2) it is also apparent that one ferrocenyl unit and one phenyl group lie toward the half of the coordination plane of Ru comprising the two chlorides, while the remaining part of the ligand backbone lies on the other side. The Ru−P and Ru−Cl bond distances in **14**·2CH_2Cl_2 are in the range normally observed for mononuclear Ru(II) dichloride complexes with tridentate phosphines.[24,32,37−40]

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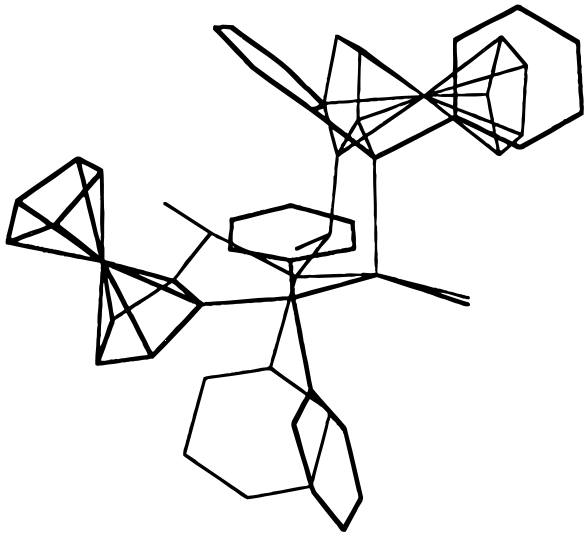
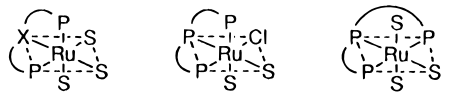


Figure 2. Schematic representation of the solid-state structure of the complex [(*S*)-(*R*)-Pigiphos]$RuCl_2 \cdot 2CH_2Cl_2$ (**14**$\cdot 2CH_2Cl_2$). Dichloromethane molecules are omitted for clarity.

Chart 2



21-23,25 **20,24** **19**

S = NCMe, X= P,S

It is worth noticing that the (*S*)-(*R*)-Pigiphos ligand is able to adopt either a *fac* (as in **14**) or a *mer* (as in **19**) coordination geometry. Square-planar complexes of (*S*)-(*R*)-Pigiphos (see {[(*S*)-(*R*)-Pigiphos]PdCl}PF_6[6] and {[(*S*)-(*R*)-Pigiphos]Rh(CO)}OTf[41]) have also been reported.

Synthesis and Characterization of Chiral Ruthenium Acetonitrile Chloride Complexes. Stable, cationic MeCN adducts of the general formula $[(L)RuCl_{2-x}(CH_3CN)_{x+n}]^{x+}$ (L = bis(ferrocenyl) tridentate ligand; $x = 1, 2$; $n = 0, 1$; **20**−**25**) can be isolated by treatment of the corresponding chloride complexes in MeCN with any halide scavenger such as $TlPF_6$. With 2 equiv of the latter reagent, *fac* tris(acetonitrile) dicationic complexes (**21**−**23**, **25**) and *fac* bis(acetonitrile) monocationic (**24**) complexes can be obtained (Chart 2). The maintainment of the *fac* arrangement by the tridentate ligands as one goes from chloride to acetonitrile complexes has several precedents in Ru(II) coordination chemistry.[32]

Reaction of $[Ru(NBD)(CH_3CN)_4](BF_4)_2$ with (*S*)-(*R*)-Pigiphos (**8**) in refluxing toluene gave the *mer* isomer **19** of complex **21** (Chart 2). The long time required by this reaction to give satisfactory yields of **19** (18 h for a 38% yield) induced us to discard this synthetic procedure with the other tridentate ligands.

All the acetonitrile adducts are orange microcrystalline solids that are quite stable in deaerated CH_2Cl_2 solution. The solid-state IR spectra contain absorptions in the region 2355−2285 cm^{-1}, where ν(C−N) signals for coordinated MeCN are usually found.[32,42,43]

$^{31}P\{^1H\}$ NMR data for the complexes **19**−**25** in CD_2Cl_2 are reported in Table 3, and selected ^1H NMR data are reported in the Experimental Section. All compounds are stereochemically rigid on the NMR time scale at room temperature. A *fac* arrangement of the ligands can be proposed on the basis of the AMQ patterns, which show J_{PP} values of ca. 30 Hz.[22,23]

In the tris(acetonitrile) complexes **21**−**23** the separations of the ^{31}P signals are comparable (*ca.* ±10 ppm) to those of the corresponding free ligands, a finding that is consistent with three identical ligands *trans* to the phosphorus atoms. Analogous spectra have been reported for several acetonitrile complexes $[L_3Ru(CH_3CN)_3]^{2+}$ (L = phosphine; L_3 = tridentate phosphine ligand).[32,43]

Consistent with the *mer* arrangement of the ligand, the ^{31}P NMR spectrum of **19** shows a second-order AMN spin system with a $J_{P_AP_B}$ value of 264.5 Hz, indicative of a *trans* disposition of the terminal phosphorus. The ^{31}P chemical shifts of the two PhP nuclei in **19** are shifted upfield by ca. 11 ppm as compared to the corresponding resonances of the *fac* isomer **21**, likely due to the strong *trans* influence of the two phosphine groups.[24,27]

Though the *mer* complex **19** should be thermodynamically more stable than its *fac* isomer due to steric factors,[24,44] no *fac*−*mer* isomerization is seen by ^{31}P NMR spectroscopy in either CH_2Cl_2 or CH_3CN in the temperature range from 21 to 100 °C. *fac* → *mer* isomerizations have previously been observed in solution for related complexes with tridentate ligands.[24]

The characteristic ^1H and ^{13}C NMR resonances of the acetonitrile molecules in all complexes can readily be assigned by means of ^1H,^{13}C correlations (Table 5). Due to the small contribution of the neighbor anisotropy effect,[23,45] ^{13}C chemical shifts generally provide more direct information concerning the electronic environment of a given ligand than proton shifts do. In particular, the differences in the ^{13}C chemical shifts are a measure of the differing electronic environments for these nuclei.[46] In complexes **19**−**25**, the observed shift to lower field by ca. 4 and 10 ppm for the CH_3CN and CH_3CN carbon resonances, respectively, as compared to the corresponding resonances of free acetonitrile (0.3 and 117.2 ppm) is thus unequivocally indicative of coordinated acetonitrile molecules. In particular, we attibute a $\Delta\delta(CH_3) > 3.7$ ppm to the acetonitrile

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Table 5. ^{1}H and ^{13}C NMR Data for the Coordinated CH_3CN Molecules of the Acetonitrile Complexes[a]

	$(CH_3CN)^I$			$(CH_3CN)^{II}$			$(CH_3CN)^{III}$		
complex	$\delta(^1H)$	$\delta(^{13}C)$		$\delta(^1H)$	$\delta(^{13}C)$		$\delta(^1H)$	$\delta(^{13}C)$	
19	2.53 (s)	4.43; $^1J = 139.4$	125.60; $^2J = 10.4$	2.36 (s)	5.74; $^1J = 137.9$	129.60; $^2J = 10.4$	1.20 (s)	3.81; $^1J = 139.2$	125.80; $^2J = 11.3$
21	2.27 (s)	4.25; $^1J = 138.3$	127.26; $^2J = 9.8$	2.10 (s)	4.59; $^1J = 138.9$	127.21; $^2J = 9.3$	1.70 (s)	3.14; $^1J = 140.1$	126.46; $^2J = 10.8$
22	2.38 (s)	4.27; $^1J = 138.2$	127.89; $^2J = 11.3$	2.02 (s)	4.24; $^1J = 138.9$	126.66; $^2J = 10.4$	1.78 (s)	3.00; $^1J = 139.0$	125.44; $^2J = 10.8$
23	2.44 (s)	4.14; $^1J = 138.9$	130.12; $^2J = 10.8$	2.07 (s)	4.33; $^1J = 139.7$	128.02; $^2J = 10.8$	1.79 (s)	3.54; $^1J = 138.2$	126.87; $^2J = 10.7$
24	2.03 (s)	4.17; $^1J = 139.8$	126.02; $^2J = 9.9$	1.77 (s)	3.40; $^1J = 140.4$	124.60; $^2J = 11.5$			
25[b]	2.15 (s)	3.92; $^1J = 139.6$	128.36; $^2J = 9.8$	1.81 (s)	3.05; $^1J = 137.9$	124.86; $^2J = 9.9$	1.37 (s)	2.76; $^1J = 139.5$	123.60; $^2J = 10.4$

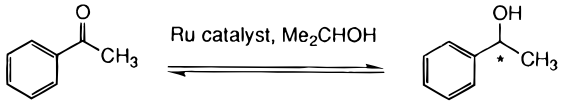
[a] 500.13 MHz (^{1}H), 125.76 MHz (^{13}C), 294 K, CD_2Cl_2. Chemical shifts in ppm, coupling constants J_{CH} in Hz. Abbreviations: s, singlet. [b] Acetone-d_6.

Table 6. Catalytic Asymmetric Hydrogen Transfer Reactions from 2-Propanol to Acetophenone[a]

			product (1-phenylethanol)		
complex	temp (°C)	time (min)	yield (%)[b]	ee (%)[c]	config[d]
[(*S*)-(*R*)-Pigiphos]$RuCl_2$ (**14**)	25	1200	13.7	5.6	*R*
{[(*S*)-(*R*)-Pigiphos]$RuCl(CH_3CN)_2$}$^+$ (**20**)	68	90	98.3	6.6	*R*
{*fac*-[(*S*)-(*R*)-Pigiphos]$Ru(CH_3CN)_3$}$^{2+}$ (**21**)	25	1440	26.9	64.6	*R*
	68	120	99.1	71.7	*R*
	reflux	60	98.0	18.1	*R*
{[(*R*)-(*S*)-8-Me-Pigiphos]$Ru(CH_3CN)_3$}$^{2+}$ (**22**)	68	95	95.6	12.0	*R*
{[(*R*)-(*S*)-4-CF_3-Pigiphos]$Ru(CH_3CN)_3$}$^{2+}$ (**23**)	68	90	8.7	16.8	*S*
	reflux	220	50.3	21.0	*R*
{[(*S*)-(*R*)-8-CF_3-Pigiphos]$RuCl(CH_3CN)_2$}$^+$ (**24**)	reflux	170	98.6	12.0	*R*
{[(*S*)-(*R*)-S-Pigiphos]$Ru(CH_3CN)_3$}$^{2+}$ (**25**)	reflux	180	24.2	20.1	*R*
{*mer*-[(*S*)-(*R*)-Pigiphos]$Ru(CH_3CN)_3$}$^{2+}$ (**19**)	68	250	93.2	12.0	*R*

[a] Reaction conditions: complex:substrate:*i*-PrO^-K^+ = 1:100:1, solvent *i*-PrOH, Ru complex concentration *ca.* 4×10^{-3} M. For the experimental procedure see the Experimental Section. [b] Chemical yields determined by GC analysis (SPB-1 column) on the crude reaction mixture at the reported time. [c] Determined by GC analyses (Chiraldex G-TA column). [d] Determined by the sign of rotation of the isolated product.

Scheme 3



molecules *trans* to a PhP group, and a $\Delta\delta(CH_3) < 3.7$ ppm to the acetonitrile molecules *trans* to a CyP group. These $\Delta\delta$ values are easily explainable in terms of *trans* influence.[30,47] The ^{13}C chemical shifts of the CH_3CN carbons are less sensitive to the nature of the *trans* ligand; nevertheless, in the same complex the δ values for the carbons *trans* to the CyP groups generally resonate at higher field than those *trans* to the PhP groups. Following this criterion, in the bis(acetonitrile) compound **24** one acetonitrile may be located *trans* to a PhP group, while the other is *trans* to the CyP group. Interestingly, the ^{1}H,^{13}C correlations show that the phenyl rings in compound **24** undergo a restricted rotation around the P−C_{ipso} bonds at room temperature. In fact, eight separated phenyl *ortho* proton resonances (doublets, $^3J_{HP} = 8-11$ Hz) are displayed which are coupled ($^1J_{HC} = 166.8-174.4$ Hz) to eight different *ortho* carbon-13 signals. This result has been confirmed by the ^{19}F NMR spectrum, which shows eight broad singlets in the region from 63.5 to 67.0 ppm.

Reduction of Acetophenone *via* Hydrogen Transfer from Propan-2-ol. Preliminary experiments show that the cationic complexes **19**−**25** catalyze the asymmetric reduction of acetophenone to 1-phenylethanol *via* hydrogen transfer from propan-2-ol, which is also used as solvent (Scheme 3 and Table 6). To become catalytically active, however, the complexes require the presence of a basic cocatalyst such as *i*-PrOK.[48−50]

The model reaction shown in Scheme 3 has been chosen for its general occurrence in the presence of chiral Ru(II) catalysts. Indeed, asymmetric reductions of prochiral ketones can be brought about with various transition-metal catalysts through hydrogenation, hydrosilylation, or hydrogen transfer. Many effective catalyst systems comprise Ru(II) complexes with chiral phosphine, nitrogen, or oxygen donor bidentate ligands.[48,51,52] High conversions and enantiomeric excesses (>99%) have recently been obtained by Ru(II) hydrogenation catalysis in propan-2-ol with quite simple chiral diamine or amino alcohol ligands.[50h,j] Hydrogen-transfer hydrogenation of ketones catalyzed by transition-metal complexes containing tri- and tetradentate ligands have been much less intensely studied.[50g,53]

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Irrespective of the chiral bis(ferrocenyl) tridentate ligands here described, the best conversions and enantioselectivities are generally observed for the tris(acetonitrile) derivatives as well as for electron-donating groups on the phenyl substituents at the terminal phosphorus donors (Table 6). The reactions require relatively high temperatures to occur with appreciable rates (*ca.* (10^{-4} mol of product)(10^{-6} mol of catalyst) h^{-1}), while only very minor differences in rate and enantioselectivity are observed on varying the base/Ru ratio between 1 and 10. Monitoring (GC) the reaction with time at constant temperature shows that, in all cases, the ee's do not significantly depend on the total conversion of the substrate.

Complexes **19**−**22** are already efficient at 60 °C, whereas reflux temperature is required for **23** and **24**. The least active is the thioether complex **25** that even at reflux temperature gives a low conversion of acetophenone to 1-phenylethanol. The best result, in terms of both activity and enantioselectivity (ee 71.7%) has been obtained with compound **21** at 68 °C. In general, however, the ee's are low and are not comparable to those achieved with other Ru(II) chiral catalysts.[50a,h,i]

Interestingly, the conformation of the bis(ferrocenyl) ligand seems to play a key role in both the enantioface discrimination and the catalytic efficiency, as the *fac* isomer **21** (72% ee, >99% conversion in 2 h) at 68 °C is much more efficient than its *mer* isomer **19** (12% ee, 93% conversion in *ca.* 4 h). Since at reflux temperature the enantioselectivity of the *fac* isomer dramatically decreases (18% ee) to approach the value observed for the *mer* isomer, one might attribute the decrease of the enantioface discrimination to configurational instability of the *fac* catalyst precursor (*fac* → *mer* isomerization occurring at reflux temperature but not at 68 °C). Independent experiments carried out with isolated **21** apparently rule out this hypothesis, as the compound maintains the *fac* structure in MeCN solution at 100 °C. In refluxing propan-2-ol, extensive decomposition of **21** occurs, but no trace of the *mer* isomer is seen. Accordingly, we think that other causes may be responsible for the lowering of the enantioselectivity at reflux temperature.

Studies aimed at understanding the chemical and physical factors (ligand conformation, nature and basicity of the donor atoms, lability of coligands, temperature, solvent, hydrogen source) that may control the enantioselectivity of the reduction of various prochiral ketones by Ru(II) bis(ferrocenyl) tridentate complexes are presently being investigated in our laboratories.

Acknowledgment. We are grateful to G. Scapacci for technical assistance and to S. Chaloupka for an improved preparation of **2**. We are also indebted to Dr. C. Bazzicalupi for the X-ray structural analysis of **14**·CH_2Cl_2. C.B. thanks the Progetto Strategico "Tecnologie Chimiche Innovative", CNR, Italy, for financial support.

Supporting Information Available: Tables of the complete set of crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, all bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters and an ORTEP drawing of **14**·$2CH_2Cl_2$ with the complete atom labeling adopted (14 pages). Ordering information is given on any current masthead page.

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