from the 1,2-diketone ligand onto the CO π orbitals through the metal d_{yz} orbital. Such spin delocalization is evidenced by the observed ^{13}CO hf couplings. The calculation also shows that the spin delocalization onto the cyclopentadienyl group is very small, consistent with the experimental results showing no hf splittings due to the group.

Previously, Sarbasov et al. reported that the $CpMo(CO)_2$(DTBQ) complex has most of its unpaired electron on Mo. They explained it by assigning the $4d^3$ configuration to Mo and by assuming that DTBQ is coordinated to Mo as the pyrocatecholate ligand.[11] Their g and Mo hf coupling values fit on the correlation line of Figure 2 obtained for the complexes in this work. The orbital energy of the LUMO of BQ is much lower than those for AQ, PQ, and NQ (Figure 4), and hence on the basis of the reason mentioned above, the unpaired electron in the DTBQ complex is expected to be delocalized more onto the metal fragment than in the other 1,2-diketone complexes. The Sarbasov et al.'s complex, therefore, may be thought to have the same electronic configuration as in the present case. It seems interesting that in the $CpMo(CO)_2$(1,2-diketone) complexes the spin distribution is markedly affected by 1,2-diketone ligands; i.e., the spin distribution changes from the case where most of the spin is distributed on the 1,2-diketone ligand to the case where the spin is mainly distributed on the metal fragment.

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Registry No. NQ, 524-42-5; AQ, 82-86-0; PQ, 84-11-7; PPD, 579-07-7; DA, 431-03-8; FR, 492-94-4; BZ, 134-81-6; $[CpMo(CO)_3]_2$, 12091-64-4; $CpMo(CO)_2$(NQ), 114532-62-6; $CpMo(CO)_2$(PQ), 114532-63-7; $CpMo(CO)_2$(FR), 114532-64-8; $CpMo(CO)_2$(BZ), 114532-65-9; $CpMo(CO)_2$(PPD), 114532-66-0; $CpMo(CO)_2$(DA), 114532-67-1; $CpMo(CO)_2$(AQ), 114532-68-2; $CpMo(CO)(PPh_3)$(AQ), 114532-69-3; $(NQ)^-(n\text{-}Bu)_4N^+$, 114550-09-3; $(PQ)^-(n\text{-}Bu)_4N^+$, 114532-58-0; $(FR)^-(n\text{-}Bu)_4N^+$, 114532-59-1; $(BZ)^-(n\text{-}Bu)_4N^+$, 114532-60-4; $(AQ)^-(n\text{-}Bu)_4N^+$, 114532-61-5; $CpMo(CO)_2$(BQ), 114532-70-6.

Synthesis of New Chiral Ferrocenyl Amine Sulfide Complexes and Their Applications as Asymmetric Catalysts. The Structure of (*R*,*S*)-$C_5H_5FeC_5H_3[CHMeNMe_2][SCH_3][PdCl_2]$

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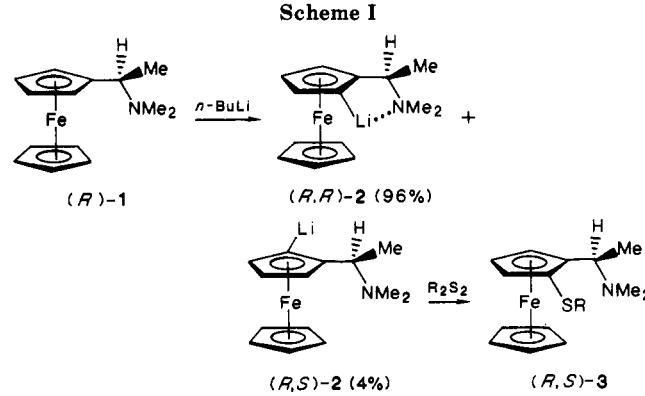
New chiral ferrocenyl sulfide ligands of the type (*R*,*S*)-$C_5H_5FeC_5H_3[CHMeNMe_2][SR]$, where R = Me, Et, *i*-Pr, *n*-Bu, *i*-Bu, *t*-Bu, *i*-Pent, Ph, CH_2Ph, *p*-tolyl, or 4-chlorophenyl, have been prepared by lithiation of optically active *N*,*N*-dimethyl-1-ferrocenylethylamine followed by reaction with the appropriate disulfide. These compounds are air-stable and readily chelate palladium and platinum chloride to form chiral heterobimetallic complexes (*R*,*S*)-$C_5H_5FeC_5H_3[CHMeNMe_2][SR][MCl_2]$ (R = Me, *i*-Pr, *n*-Pr, *i*-Bu, Ph, *p*-tolyl, 4-chlorophenyl; M = Pd, Pt). Both the ligands and the complexes were characterized by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and infrared spectroscopy. The chiral complexes are asymmetric Grignard cross-coupling catalysts. The configuration of the cross-coupling product is related to the planar chirality of the complex. The structure of (*R*,*S*)-$C_5H_5FeC_5H_3[CHMeNMe_2][SMe][PdCl_2]$ (**15**) was determined by single-crystal X-ray diffraction measurements. Compound **15** crystallizes in the orthorhombic space group $P2_12_12_1$ with lattice parameters a = 9.226 (3) Å, b = 12.219 (4) Å, c = 15.448 (5) Å, M_r 480.56, V = 1741.5 (8) Å^3, ρ(calcd) = 1.83 g/cm^3, and Z = 4. Least-squares refinement gave a final R value of 0.029 for 2175 observed ($I > 3\sigma(I)$) of 2912 unique reflections. The two cyclopentadienyl rings are eclipsed and are slightly tilted with respect to each other; the dihedral angle is 3.2°.

Introduction

Recently, we reported the synthesis of new ferrocenyl amine sulfide complexes and their catalytic applications to selective hydrogenation.[1,2] Kellogg and co-workers have also reported the catalytic application of chiral macrocyclic sulfide complexes to asymmetric Grignard cross-coupling reactions.[27] In this work, we report the synthesis of new chiral ferrocenyl sulfide ligands of the type (*R*,*S*)-$C_5H_5FeC_5H_3[CHMeNMe_2][SR]$, where R = Me, Et, *i*-Pr, *n*-Bu, *i*-Bu, *t*-Bu, *i*-pentyl, Ph, CH_2Ph, *p*-tolyl, or 4-chlorophenyl.

These compounds are easily prepared by the initial lithiation of the resolved amine **1** in a highly stereospecific manner,[3] followed by treatment of the major diastereomer of **2** with RSSR to afford (*R*,*S*)-**3** (Scheme I). These chiral ferrocenyl amine sulfides readily chelate platinum and

Scheme I



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palladium chloride to form the chiral heterobimetallic complexes to the type (R,S)-$C_5H_5FeC_5H_3[CHMeNMe_2][SR][MCl_2]$. The chiral palladium complexes are effective asymmetric Grignard cross-coupling catalysts.

Experimental Section

Air-sensitive reagents were manipulated in a prepurified argon or nitrogen atmosphere. Standard Schlenk-ware techniques and a vacuum line were employed. All chemicals were of reagent grade and were used as received. Solvents were purified and dried by standard methods[4] before use. (*R*)-*N*,*N*-Dimethyl-1-ferrocenylethylamine ((*R*)1) was prepared according to Ugi's procedure.[5]

^1H NMR spectra were obtained by use of a Bruker WM-250 spectrometer operating at 250 MHz in chloroform-d_1 solutions with chemical shifts reported in parts per million downfield from a TMS internal standard. ^{13}C NMR were obtained by use of a Bruker WM-250 spectrometer at 62.9 MHz. IR were obtained by use of a Perkin-Elmer 457 or 599 grating spectrophotometer by using Nujol mulls between CsBr plates or in KBr pellets. Mass spectra (MS) were obtained by means of a Finnigan 4000 instrument with an INCOS data system at 70 eV. Optical rotations were determined with a Perkin-Elmer 141 polarimeter. Gas chromatography was carried out by using a Hewlett-Packard 5880A instrument.

All melting points were determined by using a Thomas-Hoover capillary melting point apparatus and were uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

(*R*,*S*)-1-(1-(Dimethylamino)ethyl)-2-(methylthio)ferrocene (3, R = Me). The amine (*R*)-1 (1.5 g, 5.8 mmol) was dissolved in 50 mL of dry ether and placed in a 100-mL round-bottomed Schlenk flask equipped with a side arm and rubber septum. The solution was cooled to −78 °C, and while being stirred, 4.0 mL (6.4 mmol) of *n*-BuLi was added dropwise via syringe. The orange suspension was allowed to reach room temperature and stirred overnight. Me_2S_2 (0.53 mL, 5.9 mmol) was added dropwise via syringe at −78 °C. The solution was allowed to reach room temperature and stirred under N_2 for 24 h. After being refluxed for 7 h, the reaction mixture was cooled and then 20 mL of saturated aqueous $NaHCO_3$ was added. The resulting organic layer and ether extracts from the aqueous layer were combined, washed twice with ice water, dried over anhydrous Na_2SO_4, and evaporated to give a dark, oily residue. The oil was chromatographed on alumina by eluting first with hexane and then with CH_2Cl_2 to give the product which, upon recrystallization from hexane/petroleum ether, gave yellow crystals: yield 65%; mp 64–66 °C; MS, *m*/*e* (relative intensity) 303 (19, M^+), 213 (100, $M^+ - NMe_2$), 121 (92, FeCp), 72 (57, $CHMeNMe_2$), 56 (60, Fe); IR (Nujol, CsI) 1260, 1104, 1092, 988, 810, 450 cm^{-1}. Anal. Calcd for $C_{15}H_{21}FeNS$: C, 59.41; H, 6.93. Found: C, 59.54; H, 6.89.

(*R*,*S*)-1-(1-((Dimethylamino)ethyl)-2-(ethylthio)ferrocene (4, R = Et). The amine (*R*)-1 (1.5 g, 5.8 mmol) was dissolved in 50 mL of dry ether and placed in a 100-mL round-bottomed Schlenk flask equipped with a side arm and rubber septum. The suspension was cooled to −78 °C, and while being stirred, 4.0 mL (6.4 mmol) of *n*-BuLi was added dropwise via syringe. The orange suspension was allowed to reach room temperature and stirred overnight. Et_2S_2 (0.73 mL, 5.9 mmol) was added dropwise via syringe at −78 °C. The solution was allowed to reach room temperature and stirred under N_2 for 24 h. After being refluxed for 7 h, the reaction mixture was cooled and 20 mL of water was added. The organic layer was separated, dried, and evaporated to give a brown oil. The oil was chromatographed on alumina by gradient elution (hexane/ether/CH_2Cl_2), giving a brown oil: yield 45%; MS, *m*/*e* (relative intensity) 317 (53, M^+), 302 (23, $M^+ - CH_3$), 272 (44, $M^+ - HNMe_2$), 121 (29, FeCp), 72 (9, $CHMeNMe_2$), 56 (17, Fe), 40 (100). Anal. Calcd for $C_{16}H_{23}FeNS$: C, 60.57; H, 7.26. Found: C, 60.81; H, 7.08.

(*R*,*S*)-1-(1-(Dimethylamino)ethyl)-2-(isopropylthio)ferrocene (5, R = *i*-Pr). The procedure was the same as for **3**, except that 0.94 mL of $(i\text{-Pr})_2S_2$ (5.9 mmol) was used. The product was recrystallized from hexane to give bright orange needles: yield 80.4%; mp 34–35 °C; MS, *m*/*e* (relative intensity) 331 (85, M^+), 316 (25, $M^+ - Me$), 287 (35, $M^+ - NMe_2$), 286 (60, $M^+ - HNMe_2$), 244 (48, $M^+ - CHMeNMe_2$), 210 (5, $M^+ - CpFe$), 121 (78, FeCp), 56 (35, Fe), 43 (100, *i*-Pr; Ir (neat, KBr), 3096, 2870, 2820, 2778, 2930, 1450, 1380, 1260, 1245, 1190, 1103, 1090, 998, 930, 815, 532 cm^{-1}. Anal. Calcd for $C_{17}H_{25}FeNS$: C, 61.63; H, 7.55; S, 9.67. Found: C, 61.70; H, 7.75; S, 9.90.

(*R*,*S*)-1-(1-(Dimethylamino)ethyl)-2-(*n*-propylthio)ferrocene (6, *R* = *n*-Pr). The procedure was the same as for **3**, R = *i*-Pr, except that 0.92 mL (5.9 mmol) of $(n\text{-Pr})_2S_2$ was added. The product was recrystallized from hexane/CH_2Cl_2 to give dark orange crystals; yield 65%; mp 32.3 °C; MS, *m*/*e* (relative intensity) 331 (100, M^+), 316 (36, $M^+ - Me$), 288 (13, $M^+ - n\text{-Pr}$), 287 (48, $M^+ - NMe_2$), 286 (71, $M^+ - HNMe_2$), 256 (5, $M^+ - S\text{-}n\text{-Pr}$), 210 (5, $M^+ - FeCp$), 121 (17, FeCp), 65 (3, Cp), 56 (7, Fe), 43 (38, *n*-Pr), 41 (62, $CH_2{=}CHCH_3$); IR (neat KBr) 3096, 2830, 2870, 2850, 2818, 1454, 1362, 1260, 1245, 1190, 1152, 1104, 998, 950, 815, 454 cm^{-1}. Anal. Calcd for $C_{17}H_{25}FeNS$: C, 61.63; H, 7.55. Found: C, 61.90; H, 7.62.

(*R*,*S*)-1-(1-(Dimethylamino)ethyl)-2-(*tert*-butylthio)ferrocene (7, R = *t*-Bu). The amine (*R*)-1 (1.0 g, 3.9 mmol) was dissolved in 40 mL of dry ether in a 100-mL rond-bottomed Schlenk flask equipped with a side arm and rubber septum. The suspension was cooled to −78 °C, and while being stirred 1.8 mL of 2.7 M *n*-BuLi (4.8 mmol) was added dropwise via syringe. The orange suspension was allowed to reach room temperature and stirred overnight. Then 0.78 mL of $t\text{-Bu}_2S_2$ (4.0 mmol) was added dropwise via syringe at −78 °C. The reaction mixture was allowed to reach room temperature and stirred under N_2 for an additional 24 h, after which saturated aqueous $NaHCO_3$ was added to the mixture. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with cold water, and dried over anhydrous K_2CO_3. Evaporation of the solvent gave a brown oil that was chromatographed on a silica gel column by eluting first with hexane, then with ether, and finally with MeOH. The product obtained was orange oil: yield 64%; MS, *m*/*e* (relative intensity) 345 (35, M^+), 301 (5, $M^+ - NMe_2$), 300 (5, $M^+ - HNMe_2$), 244 (100, $M^+ - t\text{-Bu} - NMe_2$), 121 (131, FeCp), 89 (4, S-*t*-Bu), 57 (33, *t*-Bu), 56 (15, Fe); IR (neat, CsI) 3100, 2960, 2940, 2860, 2820, 1450, 1390, 1370, 1260, 1245, 1190, 1000, 930, 818, 656, 468 cm^{-1}. Anal. Calcd for $C_{18}H_{27}FeNS$: C, 62.61; H, 7.83. Found: C, 62.70; H, 8.00.

(*R*,*S*)-1-(1-(Dimethylamino)ethyl)-2-(isobutylthio)ferrocene (8, R = *i*-Bu). The procedure was the same as for **7**, R = *t*-Bu, except that 0.75 mL (4.0 mmol) of $i\text{-Bu}_2S_2$ was used. The product was obtained as brownish orange oil: yield 84.5%; MS, *m*/*e* (relative intensity) 345 (80, M^+), 330 (28, $M^+ - Me$), 301 (38, $M^+ - NMe_2$), 300 (42, $M^+ - HNMe_2$), 256 (3, $M^+ - S\text{-}i\text{-Bu}$), 244 (24, $M^+ - NMe_2 - i\text{-Bu}$), 121 (36, FeCp), 89 (6, S-*i*-Bu), 72 (100, $HCMeNMe_2$), 65 (5, Cp), 57 (26, *i*-Bu), 56 (48, Fe), 45 (16 $HNMe_2$), 44 (34, NMe_2); IR (neat, CsI) 3100, 2960, 2940, 2870, 2820, 1460, 1383, 1365, 1260, 1190, 1106, 1000, 818, 532, 496, 452 cm^{-1}. Anal. Calcd for $C_{18}H_{27}FeNS$: C, 62.61; H, 7.83. Found: C, 62.81; H, 7.99.

(*R*,*S*)-1-(1-(Dimethylamino)ethyl)-2-(*n*-butylthio)ferrocene (9, R = *n*-Bu). The procedure was the same as for **7**, R = *t*-Bu, except that 0.76 mL (4.0 mmol), of $n\text{-Bu}_2S_2$ was used. The product was obtained as brownish orange oil: yield 81.2%; MS, *m*/*e* (relative intensity) 345 (91, M^+), 330 (31, $M^+ - Me$), 302 (11, $M^+ - Pr$), 301 (48, $M^+ - NMe_2$), 300 (51, $M^+ - HNMe_2$), 256 (5, $M^+ - SBu$), 121 (42, FeCp), 65 (6, Cp), 56 (48, Fe), 45 (20, $HNMe_2$), 44 (42, NMe_2); IR (neat, CsI) 3100, 2970, 2940, 2860, 2820, 1460, 1380, 1265, 1245, 1190, 1106, 1000, 818, 532, 452 cm^{-1}. Anal. Calcd for $C_{18}H_{27}FeNS$: C, 62.61; H, 7.88. Found: C, 62.50, H, 8.00.

(*R*,*S*)-1-(1-(Dimethylamino)ethyl)-2-(isopentylthio)ferrocene (10, R = *i*-Pent). The procedure was the same as **7**, except that 0.5 g (1.95 mmol) of the amine (*R*)-1 and 0.41 g (1.99 mmol) of $(i\text{-Pent})_2S_2$ was used. The product was obtained as a light brown oil: yield 72%; MS, *m*/*e* (relative intensity) 359 (60,

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M^+), 344 (20, M^+ – Me), 315 (25, M^+ – NMe_2), 314 (32, M^+ – $HNMe_2$), 121 (10, FeCp), 103 (8, SPent), 56 (12, Fe). Anal. Calcd for $C_{19}H_{29}FeNS$: C, 63.51; H, 8.08. Found: C, 63.73; H, 7.92.

(*R*,*S*)-1-(1-(Dimethylamino)ethyl)-2-(phenylthio)ferrocene (11, R = Ph). The amine (*R*)-1 (1.5 g, 5.8 mmol) was dissolved in 50 mL of dry ether and placed in a 200-mL round-bottomed flask equipped with a side arm and rubber septum. The suspension was cooled to −40 °C, and 4.0 mL (6.4 mmol) *n*-BuLi was added slowly via syringe. The orange suspension was allowed to reach room temperature and stirred overnight. Ph_2S_2 (1.29 g, 5.91 mmol), dissolved in 30 mL of warm hexane, was added dropwise via cannula to the orange suspension at −78 °C. The resulting solution was allowed to reach room temperature and then refluxed overnight under N_2. When the reaction mixture was cooled to room temperature, 30 mL of H_2O was added. The resulting organic layer was separated, dried, and evaporated to give a dark, oily residue. Unreacted Ph_2S_2 was removed by sublimation. The oil was chromatographed on activated alumina by eluting first with hexane and then with CH_2Cl_2 to give the product, which was recrystallized from hexane/CH_2Cl_2 to give orange crystals: yield 85%; mp 70–72 °C; MS, *m/e* (relative intensity) 365 (70, M^+), 320 (78, M^+ – $HNMe_2$), 212 (31, vinylferrocene), 121 (54, FeCp), 72 (100, $CHMeNMe_2$), 56 (45, Fe). Anal. Calcd for $C_{20}H_{23}FeNS$: C, 65.75; H, 6.30. Found: C, 65.32; H, 6.21.

(*R*,*S*)-1-(1-(Dimethylamino)ethyl)-2-(benzylthio)ferrocene (12, R = CH_2Ph). The procedure was the same as for **11**, R = Ph, except that 1.45 g (5.88 mmol) of $(PhCH_2)_2S_2$ was used. The product was obtained as a brown oil: yield 75%. MS, *m/e* (relative intensity) 379 (25, M^+) 334 (54, M^+ – $HNMe_2$), 244 (39), 121 (57, FeCp), 91 (100, CH_2Ph), 72 (84, $CHMeNMe_2$), 56 (Fe); IR (neat) 3090–3000, 1490, 1000, 456 cm^{-1}. Anal. Calcd for $C_{21}H_{25}FeNS$: C, 66.49; H, 6.60. Found: C, 66.52; H, 6.65.

(*R*,*S*)-1-(1-(Dimethylamino)ethyl)-2-(*p*-tolylthio)ferrocene (13, R = *p*-Tolyl). The procedure was the same as for **11**, except that 0.5 g (1.95 mmol) of the amine (*R*)-1 and 0.48 g (1.94 mmol) of *p*-tolyl disulfide was used. The product was obtained as yellow crystals upon recrystallization from hexane/CH_2Cl_2: yield 85%; mp 66–67 °C; MS *m/e* (relative intensity) 379 (81, M^+), 364 (27, M^+ – CH_3), 335 (52, M^+ – NMe_2), 334 (19, M^+ – $HNMe_2$), 121 (90, FeCp), 72 (100, $CHMeNMe_2$), 56 (55, Fe). Anal. Calcd for $C_{21}H_{25}FeNS$: C, 66.49; H, 6.60. Found: C, 66.25; H, 6.82.

(*R*,*S*)-1-(1-(Dimethylamino)ethyl)-2-((4-chlorophenyl)thio)ferrocene (14, R = 4-Chlorophenyl). The procedure was the same as for **11**, except that 1.0 g (3.89 mmol) of the amine (*R*)-1 and 1.12 g (3.9 mmol) of 4-chlorophenyl disulfide was used. The product was obtained as yellowish orange crystals upon recrystallization from CH_2Cl_2/petroleum ether: yield 72%; mp 97–98 °C; MS, *m/e* (relative intensity) 399.5 (21, M^+), 355 (27, M^+ – NMe_2), 354 (20, M^+ – $HNMe_2$), 143 (7, S-4-chlorophenyl), 121 (75, FeCp), 72 (100, $HCMeNMe_2$), 56 (55, Fe), 44 (34, NMe_2); IR (KBr pellet) 3100–3050, 2970, 2930, 2820, 1575, 1185, 1001, 470 cm^{-1}. Anal. Calcd for $C_{20}H_{22}FeNSCl$: C, 60.08; H, 5.51. Found: C, 59.89; H, 5.39.

Synthesis of Metal Complexes. The complexes (*R*,*S*)-$C_5H_5FeC_5H_3[CHMeNMe_2][SR][MCl_2]$ (R = Me, *i*-Pr, *n*-Pr, *i*-Bu, Ph, *p*-tolyl, 4-chlorophenyl; M = Pd, Pt) were prepared from benzene solutions of the appropriate $(PhCN)_2MCl_2$[6] species and a slight excess of the ferrocenylamine sulfide ligand in an approximate 1:1.1 molar ratio. The reaction mixture was stirred for 10 h in the case of Pd complexes and for a week in the case of Pt complexes. The resulting precipitates were filtered, washed with benzene and then with petroleum ether, and recrystallized from CH_2Cl_2/hexane by slow evaporation.

Grignard Cross-Coupling Reaction of Allylmagnesium Chloride to 4-Phenyl-1-pentene Using the Metal Complexes. The catalyst (0.0499 mmol) was placed in a 100-mL round-bottomed Schlenk flask equipped with a stirring bar and a septum. The vessel was evacuated and filled with Ar several times. After being cooled to −78 °C, the reaction vessel was charged with 1.41 g (10.0 mmol) of 1-phenylethyl chloride in 20 mL of dry ether and stirred for 2 h at room temperature before addition of allylmagnesium chloride (20 mmol, 10 mL of a 2 M solution in THF) via syringe at −78 °C. The reaction mixture was allowed to warm to 0 °C, stirred for 40 h, and hydrolyzed with 10% HCl. The organic layer and ether extracts from the aqueous layer were combined, washed with saturated $NaHCO_3$ solution and water, and dried over Na_2SO_4. Evaporation of solvent and chromatography on a silica gel column (hexane/CH_2Cl_2) gave the product 4-phenyl-1-pentene.

Conversion of 4-Phenyl-1-pentene to Methyl 3-Phenylbutyrate. The procedure adopted for this conversion was similar to that reported by Kumada.[25] To a solution of 4-phenyl-1-pentene (0.453 g, 3.1 mmol) in 80 mL of *tert*-butyl alcohol were added a solution of 1.24 g (9.0 mmol) of K_2CO_3 in 60 mL of water and a solution of 5.13 g (24 mmol) of sodium periodate and 0.63 g (4.0 mmol) of $KMnO_4$ in 60 mL of water. The solution was adjusted to pH 8.5 with 2 N aqueous NaOH and was stirred overnight. After *tert*-butyl alcohol was removed under reduced pressure, the aqueous solution was acidified with concentrated HCl to pH 2.5, and sodium bisulfite was added until the solution became off-white. The solution was extracted with ether, and the extracts were dried over Na_2SO_4, concentrated, and distilled [120–135 °C (2 mm)]. A solution of the acid thus obtained (0.295 g, 1.8 mmol) and *p*-toluenesulfonic acid (940 mg) in 10 mL of methanol was refluxed for 3 h. The solvent was removed under reduced pressure, and the residue was taken up in ether. The solution was washed with 10% aqueous NaOH, dried over anhydrous Na_2SO_4, and evaporated. The residue was distilled [110–130 °C (2 mm)] to give about 72–85% of methyl 3-phenylbutyrate: ^1H NMR (δ) 1.29 (d, J = 7.0 Hz, 3 H, $CHCH_3$), 2.53 (dd, J_{gem} = 15 Hz, J_{vic} = 8 Hz, 1 H, CH_2CH), 2.63 (dd, J_{gem} = 15 Hz, J_{vic} = 8 Hz, 1 H, CH_2CH), 3.28 (sex., J = 7.0 Hz, 1 H, CH_2CHPhMe), 3.61 (s, 3 H, OCH_3), 7.17–7.45 (m, 5 H, Ph).

X-ray Analysis of Dichloro[(*R*,*S*)-(1-(2-(methylthio)-1-ferrocenyl)ethyl)dimethylamine]palladium(II) (15). A deep purple pyramidal crystal of **15**, $C_{15}H_{21}Cl_2FeNPdS$, having approximate dimensions of 0.20 × 0.25 × 0.45 mm, was mounted in a glass capillary in a random orientation. Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.710 73 Å) on a Nicolet P3F diffractometer equipped with a graphite crystal incident beam monochromator.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement by using the setting angles of 20 reflections in the range $35 < 2\theta < 39°$. The orthorhombic cell parameters and calculated volume are a = 9.226 (3) Å, b = 12.219 (4) Å, c = 15.448 (5) Å, and V = 1741.5 (8) Å^3. For Z = 4 and M_r 480.56, the calculated density is 1.83 g/cm^3. From the systematic absences of $h00$, $h = 2n + 1$, $0k0$, $k = 2n + 1$, and $00l$, $l = 2n + 1$ and from subsequent least-squares refinement, the space group was determined to be $P2_12_12_1$.

The data were collected at a temperature of 23 (1) °C by the θ–2θ scan technique. The scan rate varied from 4 to 30°/min (in 2θ). Data were collected to a maximum 2θ of 60°. The scan range (in deg) was determined as a function of 2θ to correct for the separation of the kα doublet,[7] the scan width was calculated as follows: 2θ scan width = 2.00 + (2θ(Kα_2) − (2θ(Kα_1)). The ratio of peak counting time to background counting time was 1:1. The diameter of the incident beam collimator was 1.0 mm and the crystal to detector distance was 19 cm. A total of 2937 reflections were collected, of which 2912 were unique and not systematically absent. A linear-decay correction was applied with correction factors on I ranging from 1.000 to 1.003 and with an average value of 1.002.

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 22.7 cm^{-1} for Mo Kα radiation. An empirical absorption correction, based on a series of psi scans, was applied to the data. Relative transmission coefficients ranged from 0.892 to 0.999 with an average value of 0.959. No secondary extinction correction was applied.

The structure was solved by using the Patterson heavy-atom method that revealed the position of the Pd atom. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located, and their positions and isotropic thermal parameters were refined.

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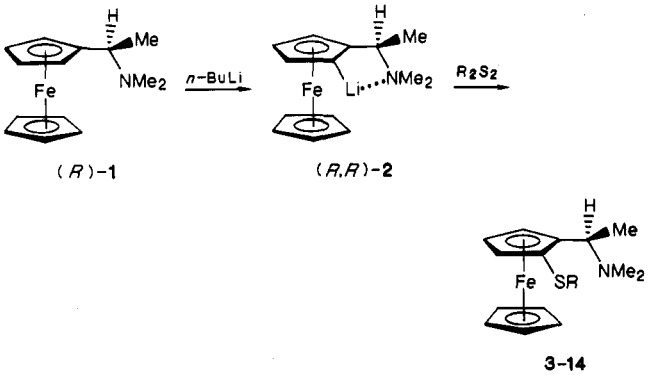
(7) *Data Collection Operation Manual*; Nicolet XRD Corp., 1980.

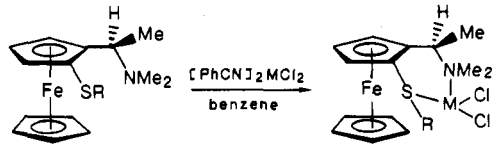
Scheme II



(R)-1 (R,R)-2 3-14

R = Me, Et, *i*-Pr, *n*-Pr, *n*-Bu, *i*-Bu, *t*-Bu, *i*-Pent, Ph, CH_2Ph, *p*-tolyl, 4-chlorophenyl (4-ClPh)

Scheme III



R,S ligands

15: M = Pd, R = Me
16: M = Pd, R = *i*-Pr
17: M = Pd, R = *n*-Pr
18: M = Pd, R = *i*-Bu
19: M = Pd, R = Ph
20: M = Pd, R = *p*-tolyl
21: M = Pd, R = 4-ClPh
22: M = Pt, R = 4-ClPh

Scattering factors were taken from Cromer and Waber.[8] Anomalous dispersion effects were included in F_c;[9] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[10] Only the 2175 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 275 variable parameters and converged with unweighted and weighted agreement factors of $R_1 = R_2 = 0.029$. The standard deviation of an observation of unit weight was 1.29 The highest peak in the final difference Fourier had a height of 0.59 e/Å^3 with an estimated error based on $\sigma(F)$ of 0.09.[11] Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices showed no unusual trends. The molecular chirality was established as attempts to refine the opposite enantiomorph led to significantly larger values for $R_1 = 0.032$, $R_2 = 0.032$, and the standard deviation of an observation of unit weight = 1.410.

All calculations were performed on a VAX-11 computer using SDP-PLUS.[12] A summary of bond lengths and angles are given in Tables V and IX, respectively.

Results and Discussion

New chiral ferrocenyl amine sulfide ligands of the type (*R*,*S*)-$C_5H_5FeC_5H_3[CH(CH_3)N(CH_3)_2][SR]$, where R = Me, Et, *i*-Pr, *n*-Pr, *n*-Bu, *i*-Bu, *t*-Bu, *i*-Pent, Ph, CH_2Ph, *p*-tolyl, or 4-ClPh, have been prepared in a general, high-yield, one-step synthesis shown in Scheme II. The starting material (*R*)-*N*,*N*-dimethyl-1-ferrocenylethylamine [(*R*)-**1**] was prepared from ferrocene according to Ugi's procedure[5] and was resolved by using (*R*)-(+)-tartaric acid. As illustrated by Ugi,[13] the (*R*)-amine [(*R*)-**1**] is stereoselectively lithiated by *n*-butyllithium to give 96% of the (*R*,*R*)-**2**. The *R*,*R* derivative is thought to be stabilized by the coordination of the adjacent nitrogen atom (in the side chain) to the lithium atom. The lithiated chiral ferrocene derivative is then treated with the appropriate disulfides to produce the product as (*R*,*S*)-amines. In some cases (as in preparation of the phenyl derivative), it may be necessary to reflux the reaction mixture before workup. The chiral ferrocenyl amine sulfide products **3–14** are usually deprotonated by washing with aqueous $NaHCO_3$ before separaton by chromatography on an alumina or silica gel column. It should be noted here that the chiral ferrocenyl amine sulfide compounds **3–14** contain two elements of chirality. The *R* configuration refers to the asymmetric carbon while the *S* configuration refers to the planar chirality. The yields of these products are fairly high (ranging from 45% yield in the ethyl derivative to 85% yield in the *p*-tolyl derivative) due to the modified procedure adopted.[14] The (*R*)-*N*,*N*-dimethyl-1-[(*R*)-2-lithioferrocenyl]ethylamine [(*R*,*R*)-**2**] was not isolated here but rather was prepared fresh for each reaction.

The 250-MHz ^{1}H NMR data for the chiral ferrocenyl amine sulfide ligands **3–14** are given in Table I. The ^{1}H NMR spectra of these compounds are typical of 1,2-unsymmetrically disubstituted ferrocenes in which one of the rings is unsubstituted. Rosenblum and Woodward[15] have shown that there is free rotation about the Fe–Cp axis in ferrocenes. The barrier to rotation in ferrocene is only about one-third that of the two methyl groups in ethane.[15] Consequently, the unsubstituted C_5H_5 ring appears as a singlet at 4.06–4.17 ppm region. Another striking feature of these spectra is the diastereotopic nature of the SCH_2 protons. The two methylene protons appear at different positions with their appropriate multiplicity. In the case of the isopentyl derivative (*R*,*S*)-**10**, the total number of peaks expected from the methylene protons should be $2(2^3) = 16$. However, the actual number observed was 15 due to overlap of the central peaks.

The upfield peaks (1.90–2.12 ppm) of NMe_2 in these compounds are due to the ring-current effect. The inversion of the pyramidal N of NMe_2 is faster than the NMR time scale at room temperature, so that nitrogen methyls appear as singlet in these compounds. Assignments of the disubstituted ring protons H_3, H_4, and H_5 cannot be made with absolute certainty since a number of ^{1}H NMR studies[17,18] have shown that a single substituent may deshield or shield positions 3 and 4 in any combination relative to ferrocene. However, tentative assignments for H_3, H_4, and H_5 have been given in Table I, and deuteriation studies may be necessary to make them unambiguous.

The ^{13}C NMR data for the chiral ferrocenyl amine thioether ligands **3–14** are presented in Table II. Koridze[19]

(8) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.
(9) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.
(10) Cromer, D. T. *International Tables for X-Ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.
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(12) Frenz, B. A. *The Enraf-Nonius CAD 4 SDP—A Real-time System for Concurrent X-ray Data Collection and Crystal Structure Determination*; In *Computing in Crystallography*; Schenk, H., Olthof-Hazelkamp, R., vanKonigsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.
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Table I. 250-MHz ^{1}H NMR Data for (*R,S*)-$C_5H_5FeC_5H_3$[CHMeNMe$_2$][SR] (R = Me, Et, *i*-Pr, *n*-Pr, *n*-Bu, I-Bu, *t*-Bu, Ph, CH_2Ph, *i*-Pent, *p*-Tolyl, 4-ClPh)[a]

							SR				
compd	Ph	C_5H_3[b]	C_5H_5	NCH	NMe_2	NCC*H*$_3$	α-H	β-H	γ-H	δ-H	$CH(CH_3)_2$ PhC*H*$_3$
(*R*)-1		4.11	4.08 s	3.60 d (6.8)	2.09 s	1.46 d					
(*R,S*)-3		4.28 t[a] 4.18 m[b,c] 4.17 m[b,c]	4.10 s	3.94 q (7)	2.13 s	1.40 d (7)	2.30 s				
(*R,S*)-4		4.20 m	4.10 s	3.95 q (7)	2.10 s	1.35 d	2.60 q 2.75 q	1.15 t			
(*R,S*)-5		4.33 t[a] 4.21 m[b,c] 4.17 m[b,c]	4.09 s	4.00 q (7)	2.12 s	1.34 d (7)	3.20 m				1.22 d (7) 1.15 d (7)
(*R,S*)-6		4.32 t[a] 4.19 m[b,c] 4.16 m[b,c]	4.10 s	3.97 q (7)	2.12 s	1.36 d (7)	2.58 q 2.77 q	1.56 m	0.95 t (7.1)		
(*R,S*)-7		4.41 t[a] 4.25 m[b,c] 4.21 m[b,c]	4.08 s	3.88 q (6.9)	2.12 s	1.30 d (6.9)		1.24 s			
(*R,S*)-8		4.29 t[a] 4.17 m[b,c] 4.13 m[b,c]	4.10 s	3.97 q (7)	2.12 s	1.35 d (7)	2.72 d 2.47 d	1.76 m	0.99 d (7) 0.93 d (7)		
(*R,S*)-9		4.31 t[a] 4.18 m[b,c] 4.15 m[b,c]	4.10 s	3.97 q (6.8)	2.12 s	1.36 d (6.8)	2.79 m 2.61 m	1.51 m	1.37 m	0.88 t	
(*R,S*)-10		4.31 t[a] 4.20 m[b,c] 4.16 m[b,c]	4.10 s	3.98 q (7)	2.10 s	1.35 d (7)	2.85 m 2.63 m	1.71 m	1.45 m	0.82–0.90 m	0.82–0.90 m
(*R,S*)-11	7.25–7.05 m	4.53 t[a] 4.42 m[b,c] 4.30 m[b,c]	4.18 s	3.85 q (7)	1.90 s	1.45 d (7)					
(*R,S*)-12	7.18 m	4.20 t[a] 4.15 m[b,c] 4.11 m[b,c]	4.06 s	4.0 q (7)	2.21 s	1.38 d (6.8)	3.90 m				
(*R,S*)-13	7.11–6.94 m	4.49 t[a] 4.30 m[b,c] 4.25 m[b,c]	4.15 s	3.86 q (7)	1.94 s	1.46 d (7)					2.24 s
(*R,S*)-14	7.12–7.04 m	4.47–4.25 m	4.17 s	3.87 q (7)	1.92 s	1.40 d (7)					

[a] Spectra obtained in $CDCl_3$/TMS at room temperature: δ (*J*, Hz). [b] a, H_3; b, H_4; c, H_5.

has assigned the signals in methoxyferrocene on the basis of deuterium-labeling studies. Since such labeling studies were not carried out in this work, most of the assignments here could be considered as tentative. However, the assignment of C_1 and C_2 in the 1,2-disubstituted cyclopentadienyl ring appear reasonable. C_2 reflects the inductive and field effects of the substituents (–SR) and exhibits the widest range of values of any of the ring carbons. The C_2 resonance in (*R,S*)-**13**, i.e., *p*-tolyl derivative, is shifted downfield by 26.1 ppm, relative to ferrocene (68.2 ppm[19]), whereas the 4-chlorophenyl derivative (*R,S*)-**14** is deshielded by 24.9 ppm. The assignments of C_1 and the unsubstituted cyclopentadienyl ring are reasonable, but assignments of C_3, C_4, and C_5 are more difficult.

Palladium and platinum complexes **15–22** were made by allowing a benzene solution of the chiral ferrocenyl amine sulfides **3**, **5**, **6**, **8**, **11**, **13** and **14** to react with bis(benzonitrile) adducts of palladium and platinum chloride salts (Scheme III). The heterobimetallic complexes are insoluble in benzene: the chiral palladium ferrocenyl amine sulfide complexes precipitate immediately while the platinum analogue precipitated after being stirred for 8 days.

The palladium complexes are soluble in acetone, CH_2Cl_2 and chloroform, except for the phenyl and tolyl derivatives which were only slightly soluble in these solvents. The platinum complex **22** is also soluble in these solvents. Analytically pure samples were obtained by the slow evaporation of the mixed-solvent system methylene chloride–petroleum ether.

Dichloro[(*R,S*)-(1-(2-(methylthio)-1-ferrocenyl)ethyl)-dimethylamine]palladium(II) (**15**) gave the best crystals as reflected in the elemental analysis and X-ray crystal structure.

The 250-MHz ^{1}H NMR data for the chiral palladium and platinum complexes **15–22** are presented in Table III. The chiral ferrocenyl amine thioether ligand undergoes a significant change in the ^{1}H NMR spectra upon complexing with platinum or palladium chlorides. Comparison of compound **3** with compound **15** shows the most striking difference in the ^{1}H NMR spectra of the complexed ligand, relative to the free ligand, is the large downfield shift of the resonance due to H_3, H_4, and H_5 of the substituted cyclopentadienyl ring. This deshielding effect was originally thought to be due to a severe tilting of the cyclopentadienyl rings where H_3, H_4, and H_5 were further from the shielding iron atom.[21] The crystal structure of the chiral methyl thioether palladium complex **15** (discussed in detail in a later section), however, indicated that the cyclopentadienyl ring was tilted 3.2° from the plane. The large downfield shift of H_3, H_4, and H_5 is due either to the magnetic anisotropy or to the inductive effect of the metal chloride. A further difference between the ^{1}H NMR spectra of the free ligand and complexed methyl ligand is the deshielding of the alkyl protons. In particular, the resonance due to sulfur methyl protons shifts from 2.30 to 2.70 ppm.

Structure of Dichloro[(*R,S*)-(1-(2-(methylthio)-1-ferrocenyl)ethyl)dimethylamine]palladium(II) (15).

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Table II. 250-MHz ^{13}C NMR Data (δ) for (R,S)-$C_5H_5FeC_5H_3$[CHMeNMe$_2$][SR] (15–22) in $CDCl_3$/TMS at Room Temperature

compd	Ph	C_2–C_5[a] C_2	C_1	C_5H_5	C_3, C_4, C_5[c]	NCH	NMe_2	SC	β-C	Ph*Me* δ-C γ-C	NCC*H*$_3$
(*R*)-**1**		68.5 d 66.5 d 66.3 d	86.2 s	67.7 d		57.8 d	40.2 q				14.8 q
(*R,S*)-**3**		84.0 s	75.1 s	69.9 d	71.0 d 67.3 d 66.5 d	56.1 d	40.5 q	19.8 q			13.1 q
(*R,S*)-**5**		94.6 s	78.3 s	69.9 d	75.2 d 67.8 d 66.7 d	55.8 d	39.9 q	39.2 d	22.6 q 23.8 q		10.6 q
(*R,S*)-**6**		93.2 s	80.5 s	69.9 d	73.3 d 67.4 d 66.5 d	55.9 d	40.2 q	38.7 t	22.9 t	13.7 q	12.0 q
(*R,S*)-**7**		95.5 s	77.8 s	70.8 d	77.7 d 68.9 d 68.2 d	55.9 d	39.9 q	45.9 s	31.7 q		9.3 q
(*R,S*)-**8**		93.2 s	80.8 s	69.9 d	73.2 d 67.4 d 66.5 d	55.9 d	40.2 q	45.9 t	28.4 d	21.7 q 22.3 q	11.8 q
(*R,S*)-**9**		93.5 s	80.5 s	69.9 d	73.5 d 67.5 d 66.5 d	55.9 d	40.2 q	36.4 t	31.8 t	13.7 q[b] 21.9 t	11.9 q
(*R,S*)-**12**	138.4 s, 129.1 d 128.3 d, 126.7 d			69.9 d	71.6 d 68.0 d 68.0 d	56.4 d	39.9 q	41.45 t			10.9 q
(*R,S*)-**13**	138.0 s 135.2 s 129.6 d 128.2 d	94.3 s	77.9 s	70.9 d	76.0 d 69.1 d 68.7 d	56.6 d	40.4 q			20.4 q	12.7 q
(*R,S*)-**14**	139.1 s 130.3 s 128.6 d 128.02 127.70 127.34	93.1 s	76.1 s	70.3 d	75.4 d 69.9 d 68.4 d	55.8 d	40.2 q				13.9 q

[a] For (*R*)-**1** only. [b] For the *n*-Bu derivative (*R,S*)-**9** only. [c] Substituted ring carbons.

Table III. 250-MHz ^1H NMR Data (δ) for (R,S)-$C_5H_5FeC_5H_3$[CHMeNMe$_2$][SR]/MCl_2 Complexes (15–22) in $CDCl_3$/TMS at Room Temperature

compd	M	Ph	C_5H_3	C_5H_5	NCH	SCH	NMe_2	NCC*H*$_3$	β-H	γ-H	Ph–CH_3 δ-CH_3
15	Pd		4.51 m 4.40 m	4.23 s	3.87 q	2.70 s	3.21 s 2.31 s	1.55 d			
16	Pd		4.63 m 4.48 m	4.27 s	3.80 q	3.88 m	3.17 s 2.24 s	1.93 d	1.75 d 1.53 d		
17	Pd		4.49 m 4.39 m	4.21 s	3.86 q	3.57 m 3.05 m	3.19 s 2.30 s	1.52 d	2.24 m 2.03 m	1.17 t	
18	Pd		4.44 m 4.39 m	4.21 s	3.83 q	3.67 d 2.82 d	3.19 s 2.33 s	1.52 d	2.37 m	1.20 d 1.18 d	
19	Pd	8.00–7.50 m	4.36 m 4.25 m 4.02 m	4.10 s	4.03 q		3.28 s 2.36 s	1.52 d			
20	Pd	7.80–7.28 m	4.33 m 4.21 m	4.00 s	3.96 q		3.16 s 2.22 s	1.44 d			2.36 s
21	Pd	8.04–7.55 m	4.68 m 4.50 m	4.12 s	4.21 q		3.18 s 2.44 s	1.50 d			
22	Pt	7.40–7.22 m	4.50–4.20 m	4.13 s	3.88 q		3.18 s 2.25 s	1.45 d			

The structure and numbering scheme of **15** is shown in Figure 1. Hydrogen atom numbers have been omitted for clarity.

The positional parameters are given in Table IV. The palladium atom is in a square-planar environment where the ferrocenyl amine thioether ligand chelates to the palladium atom through nitrogen and sulfur atoms.

The bond distances and bond angles for the complex are presented in Tables V and IX and are typical. The iron–carbon distances range from 2.021 (6) to 2.050 (6) Å with an average value of 2.034 (9) Å that compares favorably with that of 1,1′-bis(isobutylthio)ferrocene palladium dichloride.[22] The carbon–carbon distances in the cyclopentadienyl ring vary from 1.378 (12) to 1.429 (7) Å, averaging at 1.407 (17) Å, a value typical of ferrocene. The C–C–C bond angles within the two rings vary from 106.7 (7) to 109.2 (7)°, with an average angle of 108.0 (8)°, that is the typical angle for a regular, planar pentagon.

The Pd–S bond length is 2.288 (1) Å which compares favorably with the sum of the covalent radii (2.35 Å)[23] and suggests that there is little or no bonding in the Pd–S bond.

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(23) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University: Oxford, 1960.

Table IV. Positional Parameters and Their Estimated Standard Deviations for (R,S)-$C_5H_5FeC_5H_3[CHMeNMe_2][SMe]/PdCl_2$ (15)

atom	x	y	z	B,[a] Å^2
Pd1	0.24368 (4)	0.95281 (3)	0.32293 (3)	2.565 (5)
Fe1	0.72981 (8)	1.06536 (6)	0.42963 (5)	2.76 (1)
Cl1	0.1007 (2)	0.9270 (2)	0.2000 (1)	4.81 (4)
Cl2	0.1385 (2)	0.7998 (2)	0.3797 (2)	6.08 (5)
S1	0.3806 (2)	0.9739 (1)	0.44528 (9)	2.79 (2)
N1	0.3355 (5)	1.0999 (4)	0.2682 (3)	2.42 (8)
C1	0.3909 (7)	1.0741 (6)	0.1801 (4)	3.7 (1)
C2	0.2092 (7)	1.1772 (5)	0.2601 (4)	3.7 (1)
C3	0.4558 (6)	1.1545 (4)	0.3207 (4)	2.65 (9)
C4	0.5130 (9)	1.2610 (5)	0.2834 (5)	4.4 (1)
C5	0.5723 (5)	1.0719 (5)	0.3365 (3)	2.7 (1)
C6	0.7113 (6)	1.0555 (6)	0.2976 (4)	3.5 (1)
C7	0.7716 (6)	0.9588 (5)	0.3313 (4)	4.0 (1)
C8	0.6717 (7)	0.9135 (5)	0.3912 (4)	3.6 (1)
C9	0.5494 (6)	0.9827 (4)	0.3943 (3)	2.48 (9)
C10	0.740 (1)	1.2111 (5)	0.4940 (4)	4.8 (1)
C11	0.8733 (8)	1.1861 (7)	0.4558 (5)	5.0 (2)
C12	0.9229 (7)	1.0884 (7)	0.4890 (5)	5.6 (2)
C13	0.8183 (9)	1.0498 (7)	0.5498 (5)	5.8 (2)
C14	0.7074 (8)	1.1265 (7)	0.5514 (5)	5.4 (2)
C15	0.403 (1)	0.8520 (6)	0.5073 (5)	5.1 (2)
H1a	0.486 (7)	1.020 (5)	0.183 (4)	4 (1)*
H1b	0.433 (7)	1.134 (5)	0.149 (4)	4 (2)*
H1c	0.335 (6)	1.055 (5)	0.150 (4)	4 (1)*
H2a	0.179 (8)	1.196 (6)	0.316 (5)	7 (2)*
H2b	0.122 (6)	1.132 (4)	0.237 (3)	3 (1)*
H2c	0.239 (9)	1.245 (5)	0.232 (4)	6 (2)*
H3	0.411 (7)	1.171 (5)	0.370 (4)	4 (2)*
H4a	0.589 (7)	1.292 (5)	0.324 (4)	5 (2)*
H4b	0.450 (8)	1.302 (6)	0.279 (4)	6 (2)*
H4c	0.563 (6)	1.250 (4)	0.234 (3)	3 (1)*
H6	0.757 (8)	1.112 (5)	0.263 (4)	4 (1)*
H7	0.864 (6)	0.924 (4)	0.322 (4)	3 (1)*
H8	0.674 (6)	0.846 (5)	0.416 (4)	4 (1)*
H10	0.695 (7)	1.271 (5)	0.476 (4)	5 (2)*
H11	0.91 (1)	1.237 (8)	0.419 (6)	9 (3)*
H12	1.011 (7)	1.054 (5)	0.474 (4)	4 (1)*
H13	0.827 (7)	0.973 (6)	0.577 (5)	6 (2)*
H14	0.633 (7)	1.117 (5)	0.577 (4)	4 (2)*
H15a	0.329 (7)	0.824 (5)	0.523 (4)	5 (2)*
H15b	0.465 (7)	0.875 (5)	0.551 (4)	5 (2)*
H15c	0.436 (8)	0.796 (6)	0.477 (4)	6 (2)*

[a] Parameters with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table V. Bond Distances (Å) for (R,S)-$C_5H_5FeC_5H_3[CHMeNMe_2][SMe]/PdCl_2$ (15)

Pd1–Cl1	2.334 (2)	N1–C1	1.487 (7)
Pd1–Cl2	2.281 (2)	N1–C2	1.505 (8)
Pd1–S1	2.288 (1)	N1–C3	1.529 (7)
Pd1–N1	2.159 (4)	C3–C4	1.518 (9)
Fe1–C5	2.046 (5)	C3–C5	1.495 (7)
Fe1–C6	2.050 (6)	C5–C6	1.429 (7)
Fe1–C7	2.038 (6)	C5–C9	1.425 (8)
Fe1–C8	2.021 (6)	C6–C7	1.407 (9)
Fe1–C9	2.022 (5)	C7–C8	1.418 (9)
Fe1–C10	2.042 (7)	C8–C9	1.410 (8)
Fe1–C11	2.023 (8)	C10–C11	1.395 (11)
Fe1–C12	2.024 (7)	C10–C14	1.395 (10)
Fe1–C13	2.037 (7)	C11–C12	1.378 (12)
Fe1–C14	2.034 (7)	C12–C13	1.427 (11)
S1–C9	1.749 (5)	C13–C14	1.387 (11)
S1–C15	1.783 (8)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

The Pd–Cl bond, which is trans to the sulfur atom, shows no apparent trans bond lengthening, indicating that the thioether ligand has a negligible trans influence. The Pd–Cl bond distances have an average value of 2.308 (27) Å, almost equal to the sum of the Pauling covalent radii, 2.31 Å.[23] The Pd–N bond length is 2.159 (4) Å and is comparable to the sum of the Pauling covalent radii.

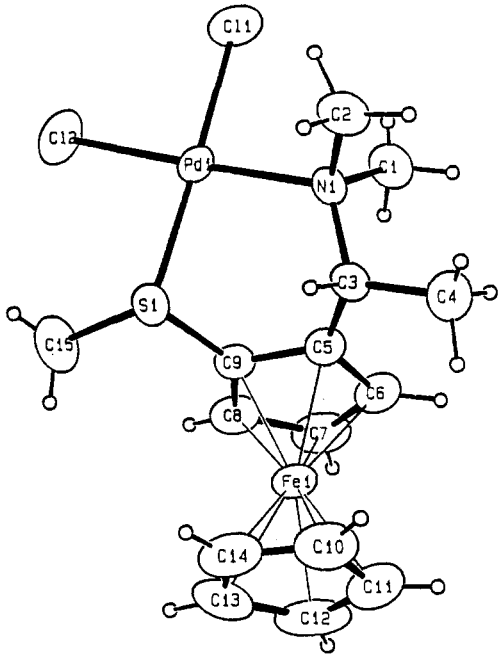


Figure 1. Structure and numbering scheme for the complex $C_5H_5FeC_5H_3[CHMeNMe_2][SMe][PdCl_2]$ (15).

Table VI. Asymmetric Grignard Cross-Coupling Reactions Using Chiral Thioether Complexes

cat.	chemical yield (%)	ee (%)	configuration
15, R = Me	97.5	26.0	*S*
16, R = *i*-Pr	95.0	22.3	*S*
19, R = Ph	96.0	18.2	*S*
20, R = *p*-tolyl	96.0	25.5	*S*
21, R = 4-ClPh	94.5	16.5	*S*

Seyferth[24] has reported a crystal structure of a heterobinuclear species $(Ph_3P)PdFe(C_5H_4S)_2$ where thiolate groups chelate to palladium. The cyclopentadienylthio groups (C_5H_4S) are tilted away from the parallel plane by 19.6°. Seyferth proposed the presence of a weak dative Fe→Pd bond on the basis of a Fe–Pd distance of 2.878 (1) Å. The structure of the methyl palladium complex **15** makes it impossible for any interaction between Pd and Fe to occur.

The two cyclopentadienyl rings are eclipsed and are slightly tilted with respect to each other; the dihedral angle is 3.2°. The planes containing the cyclopentadienyl rings are almost orthogonal to the plane containing the palladium, sulfur, nitrogen, and chlorine atoms.

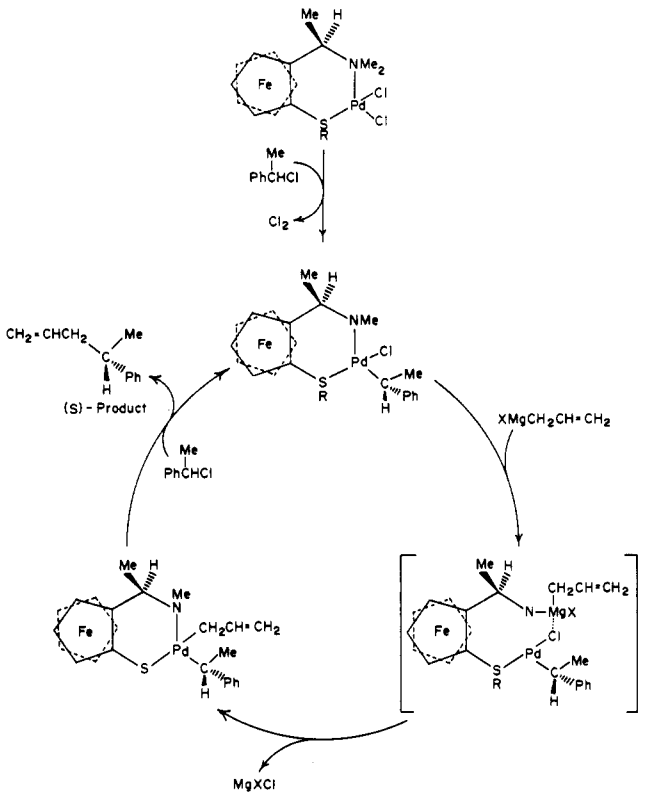
Asymmetric Grignard Cross-Coupling Studies. The new chiral ferrocenyl amine thioether palladium complexes **15**, **16**, and **19–21** were tested for asymmetric Grignard cross-coupling reactions represented below.

$$\mathrm{PhCHCl}\,(\mathrm{CH_3}) + \mathrm{ClMgCH_2CH{=}CH_2} \xrightarrow[\mathrm{Et_2O\ THF}]{\mathrm{cat.}} \mathrm{PhCH(CH_3)CH_2CH{=}CH_2}\ (>95\%)$$

The results are shown in Table VI. Since the optical rotation of the coupling product 4-phenyl-1-pentene was strongly affected by small impurities[25] and, in addition,

(24) Seyferth, D.; Hames, B. W.; Rucker, T. G.; Cowle, M.; Dickson, R. S. *Organometallics* **1983**, *2*, 472–474.
(25) Hayashi, T.; Konishi, M.;f Fukushima, M.; Kanehira, K.; Hioki, T.; Kumada, M. *J. Org. Chem.* **1983**, *48*, 2195–2202.

Scheme IV



the coupling reaction yields products which are partially racemized, it was difficult to determine the optical purity by use of a polarimeter. The alkene was converted into the methyl ester, the enantiomeric purity of which was determined by ^1H NMR spectroscopy in the presence of a chiral shift reagent, Eu(dcm)$_3$.[26] At room temperature, the ^1H NMR signal of the methyl protons of the methyl ester is a singlet when no chiral shift reagent is present. Upon addition of the shift reagent, the signal separates into two distinct singlets. The signal shifted downfield and $\Delta\Delta\delta$ increased as the concentration of the chiral shift reagent increased. When the concentration of the chiral shift reagent was 0.27 M, $\Delta\Delta\delta$ was large enough for the determination of the enantiomeric excess (ee). Kumada had reported that the methyl signal of (*S*)-methyl 3-phenylpropionate appears at a higher field than that of the *R* enantiomer.[25]

The chiral ferrocenyl amine thioether complexes with Pd **15**, **16**, and **19–21** catalyzed formation of 4-phenyl-1-pentene from 1-phenyl-1-chloroethane and allylmagnesium chloride at 0 °C in high yield (>95%). the resulting configurations in all cases were *S* (see Table VI). The enantiomeric excess (ee) range from 16.5 to 26.0 ee (*S*) and is much higher than those reported by Kellogg.[27] The Grignard cross-coupling reaction mechanism by using phosphine–amine–nickel complex was postulated by Kumada.[29] On the basis of that, we have also proposed a mechanism for the chiral thioether palladium catalyzed reaction (Scheme IV). It should be noted from our results that the configuration of the coupling product was the same as the planar chirality of the chiral ferrocenyl amine thioether palladium catalysts, although no general correlation can be drawn from this observation.

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Registry No. (*R*)-**1**, 31886-58-5; (*R*,*S*)-**3**, 100113-94-8; (*R*,*S*)-**4**, 100113-95-9; (*R*,*S*)-**5**, 100113-96-0; (*R*,*S*)-**6**, 114763-13-2; (*R*,*S*)-**7**, 114763-14-3; (*R*,*S*)-**8**, 114763-15-4; (*R*,*S*)-**9**, 100594-72-7; (*R*,*S*)-**10**, 114763-16-5; (*R*,*S*)-**11**, 100113-97-1; (*R*,*S*)-**12**, 100113-98-2; (*R*,*S*)-**13**, 100594-73-8; (*R*,*S*)-**14**, 114763-17-6; **15**, 114763-18-7; **16**, 100165-37-5; **17**, 114763-19-8; **18**, 114763-20-1; **19**, 114763-21-2; **20**, 114763-22-3; **21**, 114763-23-4; **22**, 114763-24-5; $(PhCN)_2PdCl_2$, 14220-64-5; $(PhCN)_2PtCl_2$, 14873-63-3; $PhCH(CH_3)CH_2CH{=}CH_2$, 10340-49-5; Me_2S_2, 624-92-0; Et_2S_2, 110-81-6; $(i\text{-}Pr)_2S_2$, 4253-89-8; $(n\text{-}Pr)_2S_2$, 629-19-6; $t\text{-}Bu_2S_2$, 110-06-5; $i\text{-}Bu_2S_2$, 1518-72-5; $n\text{-}Bu_2S_2$, 629-45-8; $(i\text{-}Pent)_2S_2$, 2051-04-9; Ph_2S_2, 882-33-7; $(PhCH_2)_2S_2$, 150-60-7; PhCH(Me)Cl, 672-65-1; $ClMgCH_2CH{=}CH_2$, 2622-05-1; 3-phenylbutyric acid, 4593-90-2; methyl 3-phenylbutyrate, 3461-39-0; *p*-tolyl disulfide, 103-19-5; 4-chlorophenyl disulfide, 1142-19-4.

Supplementary Material Available: Tables of general temperature factor expressions (U's), least-squares planes, bond distances involving hydrogen atoms, and bond angles factors for (*R*,*S*)-$C_5H_5FeC_5H_3$-[CHMeNME$_2$][SMe][$PdCl_2$] (8 pages); a listing of structure factors (33 pages). Ordering information is given on any current masthead page.

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