A Novel Approach to Ferrocenes with Planar Chirality

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Received July 13, 1995

Key Words: Ferrocenes, planar chiral / Deprotonation, diastereoselective / Palladium complexes / Chelating *P,N*-ligands

The 2-metalation of enantiomerically pure (*S*)-(2-methoxymethylpyrrolidin-1-yl)ferrocene FcSMP (**1**) with BuLi proceeds with high diastereoselectivity (up to 98% de) to yield the Ph_2P-substituted ferrocene (S,S_p)-**2a** after quenching with Ph_2PCl. The SMP moiety was removed by heating of **2a** at reflux in acetic anhydride to give planar chiral (S_p)-2-diphenylphosphanylferrocenylmethyl acetate (**5**). The diastereoisomer (S,R_p)-**2b** was synthesized from **1** by intermediately blocking the primary metalation site with a Me_3Si group which can be removed afterwards by treatment with KO*t*Bu in DMSO. Compound **2a** was treated with $[(C_3H_5)PdCl]_2$ to give the complex $[(C_3H_5)Pd\cdot\mathbf{2a}]PF_6$ (**7**·PF_6). The structure of **7**·PF_6 was determined by a single-crystal X-ray diffraction study and showed **2a** to act as a bidentate *P,N*-chelate ligand.

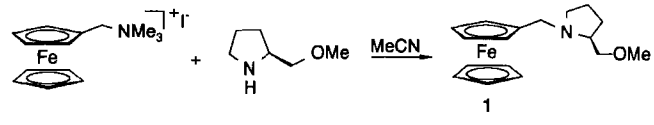
Chiral ferrocene derivatives have attracted considerable attention due to their application as ligands for asymmetric catalysis[1]. The classical route to introduce planar chirality into the ferrocene moiety was developed by Ugi et al. who utilized the diastereoselective deprotonation of optically pure 1-ferrocenylethyldimethylamine – obtained by resolution of the racemate – followed by reaction of the lithio derivative with electrophiles[2]. A great variety of compounds have since been prepared according to this methodology. Since they all contain the $CH(CH_3)X$ fragment they show both planar and central elements of chirality[3].

In contrast, the synthesis of ferrocene derivatives which only show planar chirality has been less extensively developed. Sokolov et al. succeeded in the asymmetric cyclopalladation of dimethylaminomethylferrocene in the presence of chiral amino acids[4]. Recently, a more general approach based on the diastereoselective deprotonation of chiral, ferrocenyl-substituted sulfoxides and dioxanes was presented by Kagan et al.[5]. The diastereoselective deprotonation was also applied to chiral 2-ferrocenyloxazolines[6].

In this paper we present a novel route to planar chiral 1,2-disubstituted ferrocenes which is characterized by an easy access to the substrate, highly asymmetric induction and simple replacement of the chiral auxiliary, thus enabling further derivatization.

Results and Discussion

It seemed desirable to us to start the reaction sequence with a compound featuring a ferrocenylmethyl unit $Fc-CH_2-X$, since these derivatives are readily available and the substituent X can easily be exchanged. Thus, (*S*)-(2-methoxymethylpyrrolidin-1-yl)ferrocene FcSMP (**1**) was prepared by reaction of (ferrocenylmethyl)trimethylammonium iodide with (*S*)-2-methoxymethylpyrrolidine (SMPH) – simply available from proline – in acetonitrile in 86% yield.



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The metalation of **1** was carried out with *n*BuLi in ether between −78 °C and room temperature and the lithio derivative was subsequently treated with Ph_2PCl at low temperature giving the 1,2-disubstituted ferrocene **2a** in excellent yield (Scheme 1). A phosphorus electrophile was chosen because the stereochemical outcome of the reaction could easily be analyzed by ^{31}P-NMR spectroscopy. Crude **2a** was obtained with 86% de. Changing *n*BuLi for the more reactive *sec*BuLi allows the reaction to be carried out at lower temperature and increases the diastereoselectivity to 98% de. In 1969 an asymmetric deprotonation of resolved 2-methyl-*N*-ferrocenylmethylpiperidine was published by Aratani et al.[7] but the achieved diastereoselectivity was only moderate in general, varying with the electrophile chosen, and the method was not further developed. Compound **2a** was characterized by ^1H-, ^{13}C-, ^{31}P-, $^1H/^1H$-, and $^1H/^{13}C$-NMR spectra. However, to ensure a complete assignment of the NMR signals and to further establish the applicability of the method also the minor diastereomer **2b** was prepared in pure form by the reaction sequence outlined in Scheme 1.

All compounds were obtained in >80% yield. The silylation with Me_3SiCl again proceeded with the same high degree of diastereoselectivity leading to **3** and made the second α-Cp proton available for a subsequent metalation/electrophilic quench sequence. A small amount (<15%) of the 1,1′-bis(phosphanyl)-substituted compound was formed as a byproduct of **4** which could be separated by column chromatography. The silyl group in **4** was easily removed by treatment with KO*t*Bu in DMSO. While **2a** is a powder, the

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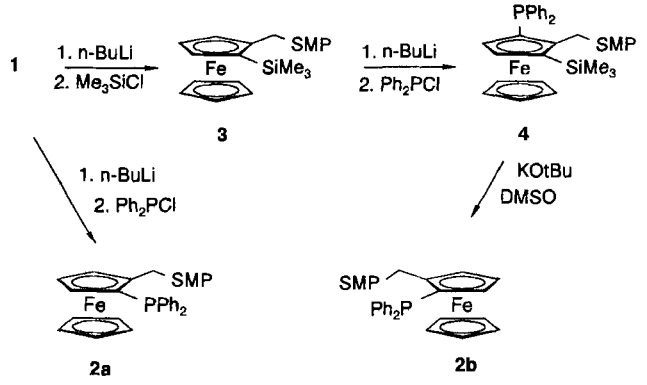
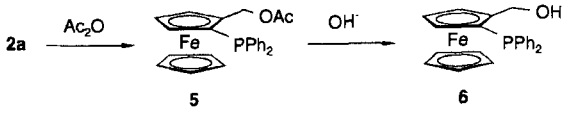
Scheme 1



isomer **2b** was obtained in crystalline form. Substitution of the SMP moiety could be achieved by heating of **2a** at reflux in acetic anhydride leading to the substituted ferrocenylmethyl acetate **5**, which was further hydrolyzed to the corresponding ferrocenylmethanol **6**.



Compound **2a** was treated with $[(C_3H_5)PdCl]_2$ to give the allyl Pd complex **7** (isolated as its hexafluorophosphate). Suitable crystals of **7** · PF_6 were obtained from CH_2Cl_2/ether and subjected to an X-ray diffraction study (Figure 1). The X-ray structure reveals the S_p configuration[8] for the planar chirality of the disubstituted Cp ring. The high diastereoselectivity in the metalation of **1** may be rationalized on the basis of an intramolecular coordination of the Li atom by the nitrogen of the SMP moiety leading preferentially to the isomer **8a**. However, due to the low inversion barrier[9] of the N atom in the SMP ring in **1** two isomers **A** and **B** are possible for the lithio derivative **8a** differing in the absolute configuration of the nitrogen center and the orientation of the SMP ring. While isomer **A** allows an additional chelation of the Li by the O atom this coordination is unlikely – as model inspection suggests – in isomer **B** because of the *trans* arrangement of the Li atom and the CH_2OMe side chain. This *N,O* chelation is known for related lithium compounds[10] and was proven to be responsible for highly asymmetric inductions in these cases. Therefore, we assume isomer **A** to be the predominant species. The coordination sphere of the Li atom might well be completed by a solvent molecule or by formation of dimeric aggregates with Li_2O_2 core. Further work will be aimed at substantiating the mode of intramolecular Li complexation.

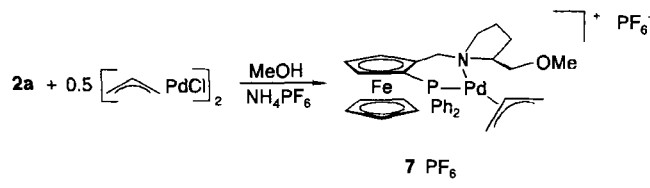
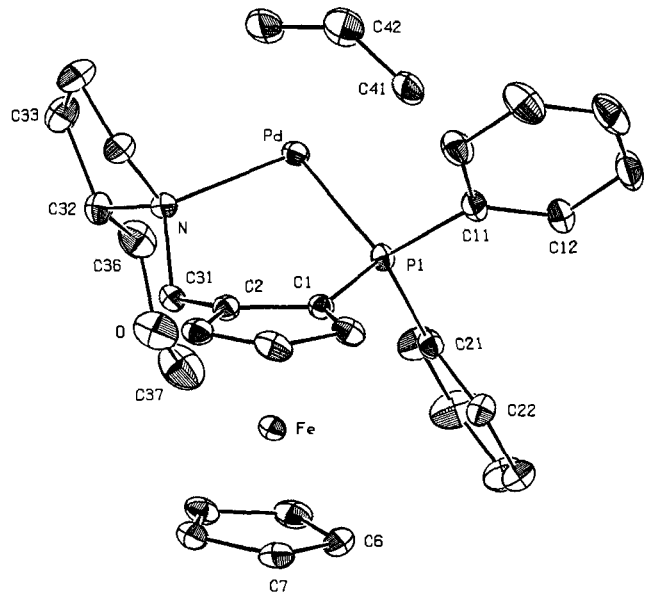
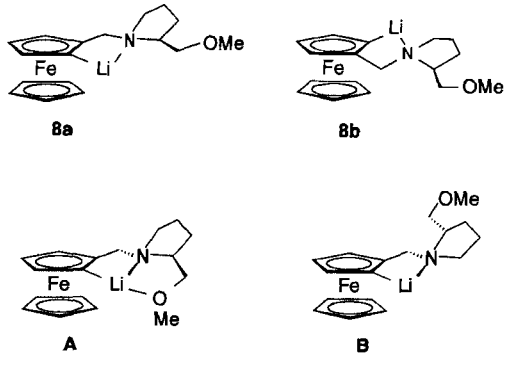


Figure 1. Molecular structure of **7**



Selected bond lengths [pm] and angles [°]: Pd–P1 230.1(1), Pd–N 221.4(3), Pd–C41 211.3(4), Pd–C43 227.1(4), Pd–C42 214.3(5), P1–C1 179.1(4), P1–C11 182.2(4), P1–C21 181.3(4), C1–C2 143.1(5), C2–C31 150.6(5), C31–N 148.6(4); P1–Pd–N 99.15(8), Pd–P1–C1 108.0(1), P1–C1–C2 121.8(3), C1–C2–C31 123.2(3), C2–C31–N 115.9(3), C31–N–Pd 110.6(2), N–Pd–C41 171.0(1), P1–Pd–C43 156.2(1), C11–P1–C21 104.5(2).



The X-ray structure shows a distorted square-planar Pd center with **2a** acting as a bidentate *P,N* chelate ligand occupying two adjacent coordination sites with the six-membered chelate ring adopting a boat conformation. The different C–C bond lengths within the allyl ligand of 135.3(8) pm (C41–C42) and 128.4(8) pm (C42–C43) together with a substantial residual electron density in the vicinity of the C_3H_5 fragment and a pronounced anisotropy of the displacement parameters of the central atom C42 suggest some disorder of the allyl ligand which is not uncommon for this class of compounds[11]. However, refinement of an additional set of positional parameters for a second allyl ligand together with an appropriate occupancy factor did not improve the quality of the structure and hence was disregarded. The *anti* configuration of the C_3H_5 moiety with respect to the CpFe group as shown in Figure 1 definitely belongs to the major isomer, the *syn* species being present with less than 25%. Interestingly, only one isomer was de-

tected in solution by NMR spectroscopy. The Pd–C bond lengths are significantly sensitive to the different *trans* effects exerted by the N and P donor centers respectively: the bond *trans* to N, Pd–C41, is 15.7 pm shorter than the Pd–C43 bond *trans* to the softer P donor atom. While the Pd–P bond length adopts a typical value[11a,12] of 230.1(1) pm the Pd–N distance of 221.4(3) pm is roughly 10 pm longer than in related compounds with oxazoline-based sp^2 N donor atoms[11]. The different donor/acceptor properties of N and P centers as manifested by the different *trans* Pd–C distances are thought to be the basis for the excellent enantioselectivities in asymmetric allylic substitutions catalyzed by (allyl)Pd complexes with *P,N*-chelate ligands[11a,13]. Hence, **7** should be a promising candidate for catalytic applications and we are currently conducting experiments to check this assumption.

We thank Prof. Dr. *G. E. Herberich* for his support.

Experimental

All manipulations were carried out under dry nitrogen in Schlenk glassware. Solvents were dried and purified by standard methods and were stored under nitrogen. – NMR: Varian Unity 500 (499.843 MHz, ^1H, int. TMS; 125.639 MHz, $^{13}C\{^1H\}$, APT, int. TMS; 202.265 MHz, $^{31}P\{^1H\}$, ext. H_3PO_4). – MS: Finnigan MAT 95. – Elemental analysis (C, H, N): Carlo-Erba elemental analyzer, Modell 1106. – SMPH[14] and (ferrocenylmethyl)trimethylammonium iodide[15] were prepared as described in the literature.

(S)-(2-Methoxymethylpyrrolidin-1-yl)methylferrocene (**1**): A mixture of (ferrocenylmethyl)trimethylammonium iodide (1.111 g, 2.88 mmol), (*S*)-methoxymethylpyrrolidine (332 mg, 3.00 mmol), and K_2CO_3 (802 mg, 5.80 mmol) in 40 ml of acetonitrile was heated at reflux for 40 h. The solid was removed by filtration, washed with CH_2Cl_2 and the solution was evaporated to dryness in vacuo. The residue was stirred with 30 ml of Et_2O, 20 ml of H_2O, and 3.0 ml of H_3PO_4 (85%). The aqueous phase was washed with two 15-ml portions of Et_2O, made alkaline (pH 10) by the addition of solid Na_2CO_3 and extracted with four 20-ml portions of CH_2Cl_2. The combined extracts were dried with Na_2SO_4 and the solvent was evaporated. The obtained crude **1** was purified by passing a hexane solution (5 ml) through a short column (3 cm) of alumina and rinsing with hexane (30 ml). Removal of the solvent in high vacuo afforded pure **1** (771 mg, 85%) as a red oil. – ^1H NMR ($CDCl_3$): δ = 1.54–1.72 (m, 3H, NCH_2CH_2); 1.81 (m, 1H, $NCHCH_2CH_2$); 2.25 (d/d/d, ^2J = 9.4 Hz, ^3J = 9.2/7.0 Hz, 1H, NCH_2CH_2); 2.62 (m, 1H, $NCHCH_2$); 2.93 (d/d/d, ^2J = 9.4 Hz, ^3J = 7.0/1.8 Hz, 1H, NCH_2CH_2); 3.23 (d/d, ^2J = 9.2 Hz, ^3J = 6.3 Hz, 1H, CH_2OCH_3); 3.34 (s, 3H, OCH_3); 3.35 (d/d, ^2J = 9.2 Hz, ^3J = 4.9 Hz, 1H, CH_2OCH_3); 3.41 (d, ^2J = 13.1 Hz, 1H, $CpCH_2N$); 3.75 (d, ^2J = 13.1 Hz, 1H, $CpCH_2N$); 4.08 (m, 2H, RC_4H_3CH); 4.10 (s, 5H, C_5H_5); 4.15 (m, 1H, RC_4H_3CH); 4.17 (m, 1H, RC_4H_3CH). – ^{13}C NMR ($CDCl_3$): δ = 22.64 (NCH_2CH_2); 28.48 ($NCHCH_2CH_2$); 53.84 ($CpCH_2N$); 54.09 (NCH_2CH_2); 59.08 (OCH_3); 61.63 ($NCHCH_2$); 67.85 (RC_4H_3CH); 67.97 (RC_4H_3CH); 68.39 (C_5H_5); 70.06 (RC_4H_3CH); 70.08 (RC_4H_3CH); 76.22 (CH_2OCH_3); 83.65 ($C_4H_4CCH_2N$). – MS (70 eV), *m/z* (%): 313 (18) [M^+], 268 (2) [$M^+ - CH_2OCH_3$], 199 (100) [$CpFeC_5H_4CH_2^+$]. – $C_{17}H_{23}FeNO$ (313.2): calcd. C 65.19, H 7.40, N 4.47; found C 64.61, H 7.45, N 4.50.

(S,S$_p$)-1-Diphenylphosphanyl-2-[(2-methoxymethylpyrrolidin-1-yl)methyl]ferrocene (**2a**): To 513 mg (1.64 mmol) of **1** in 10 ml of Et_2O at –78 °C was added 1.4 ml (1.82 mmol, 1.1 eq) of 1.3 M *sec*BuLi in cyclohexane and the mixture was stirred for 1.5 h at –78 °C and then for 1.5 h at –30 °C during which time the solution turned dark red and an orange solid precipitated. 405 mg (1.83 mmol) of Ph_2PCl was added at –78 °C and the mixture was allowed to warm to room temp. overnight. After addition of a $NaHCO_3$ solution the organic phase was separated, washed with brine, dried with Na_2SO_4 and evaporated to dryness in vacuo. Crude **2a** (98% de, ^{31}P-NMR) was chromatographed on alumina with hexane/Et_2O (4:1) as the eluent. Removal of the solvent in vacuo and crystallization of the residue from hexane at –18 °C gave 708 mg (87%) of analytically pure **2a**. – ^1H NMR ($CDCl_3$, assignments of *cis* and *trans* refer to the NCH proton and were obtained from 2D $^1H/^1H$ COSY- and NOE spectra): δ = 1.15 (m, 1H, NCH_2CH_2, *trans*); 1.25 (m, 1H, $NCHCH_2CH_2$, *trans*); 1.41 (m, 1H, NCH_2CH_2, *cis*); 1.68 (d/d/d/d, ^2J = 12.6 Hz, ^3J = 8.6/8.33/8.33 Hz, 1H, $NCHCH_2CH_2$, *cis*); 1.96 (d/d/d, ^2J = 10.0 Hz, ^3J = 9.0/6.6 Hz, 1H, NCH_2CH_2, *cis*); 2.51 (m, 1H, NCH); 2.65 (d/d, ^2J = 9.2 Hz, ^3J = 7.7 Hz, 1H, CH_2OCH_3); 2.68 (m, 1H, NCH_2CH_2, *trans*); 3.16 (d, ^2J = 12.5 Hz, 1H, $CpCH_2N$); 3.26 (s, 3H, OCH_3); 3.35 (d/d, ^2J = 9.2 Hz, ^3J = 4.3 Hz, 1H, CH_2OCH_3); 3.69 (m, 1H, RC_4H_2CH); 4.00 (s, 5H, C_5H_5); 4.20 (m, 1H, RC_4H_2CH); 4.23 (d/d, ^2J = 12.5 Hz, ^3J = 2.4 Hz, 1H, $CpCH_2N$); 4.38 (m, 1H, RC_4H_2CH); 7.18–7.56 (m, 10H, phenyl H). – ^{13}C NMR ($CDCl_3$): δ = 22.65 (NCH_2CH_2); 28.96 ($NCHCH_2CH_2$); 53.25 (d, $^3J_{C-P}$ = 8.3 Hz, $CpCH_2N$); 53.73 (NCH_2CH_2); 58.91 (OCH_3); 62.50 (NCH); 68.71 (RC_4H_2CH); 69.54 (d, J_{C-P} = 1.3 Hz, C_5H_5); 71.63 (d, J_{C-P} = 5.0 Hz, RC_4H_2CH); 72.85 (d, J_{C-P} = 3.9 Hz, RC_4H_2CH); 76.42 ($RC_4H_2CCH_2$); 76.47 (d, J_{C-P} = 2.2 Hz, CH_2OCH_3); 91.34 (d, J_{C-P} = 25.3 Hz, RC_4H_3CP); 127.37 (phenyl *p*-CH); 127.48 (d, J_{C-P} = 6.6 Hz, phenyl *o*-CH); 128.04 (d, J_{C-P} = 7.6 Hz, phenyl *o*-CH); 128.92 (phenyl *p*-CH); 132.6 (d, J_{C-P} = 18.1 Hz, phenyl *m*-CH); 135.28 (d, J_{C-P} = 20.8 Hz, phenyl *m*-CH); 138.12 (d, J_{C-P} = 8.8 Hz, RC_5H_3PC); 140.41 (d, J_{C-P} = 9.3 Hz, RC_5H_3PC). – ^{31}P NMR ($CDCl_3$): δ = –23.25. – MS (70 eV), *m/z* (%): 497 (45) [M^+], 383 (100) [$CpFeC_5H_3(CH_2)(PPh_2)^+$], 312 (10) [$M^+ - PPh_2$], 199 (40) [$CpFeC_5H_4CH_2^+$]. – $C_{29}H_{32}FeNOP$ (497.4): calcd. C 70.03, H 6.48, N 2.82; found C 70.17, H 6.68, N 2.75.

(S,S$_p$)-1-Trimethylsilyl-2-[(2-methoxymethylpyrrolidin-1-yl)methyl]ferrocene (**3**): To a solution of **1** (1.090 g, 3.48 mmol) in 10 ml of Et_2O was added with stirring 2.6 ml of 1.6 M *n*BuLi (4.16 mmol, 1.1 equiv.) at –78 °C. After 1 h at –40 °C the solution was allowed to warm to room temp. and stirring was continued for 3 h. Me_3SiCl (452 mg, 4.16 mmol) was added at –78 °C and the mixture was stirred overnight and hydrolyzed by addition of a $NaHCO_3$ solution. The organic phase was washed with brine, dried with Na_2SO_4, and the solvent was evaporated in vacuo. The residue was chromatographed on silica gel with hexane/Et_2O (1:1) to yield 1.188 g (88%) of **3** as a red oil after removal of the solvent in vacuo. – de: 93%. – ^1H NMR ($CDCl_3$): δ = 0.28 (s, 9H, $SiCH_3$); 1.45–1.65 (m, 3H, $NCH_2CH_2CH_2$); 1.85 (m, 1H, NCH_2CH_2); 2.00 (m, 1H, NCH_2CH_2); 2.55 (m, 1H, NCH); 2.71 (m, 1H, NCH_2CH_2); 3.05 (d, ^2J = 12.4 Hz, 1H, $CpCH_2N$); 3.23 (d/d, ^2J = 9.1 Hz, ^3J = 6.1 Hz, 1H, CH_2OCH_3); 3.34 (s, 3H, OCH_3); 3.47 (d/d, ^2J = 9.1 Hz, ^3J = 5.1 Hz, CH_2OCH_3); 4.01 (m, 1H, RC_4H_2CH); 4.02 (d, ^2J = 12.4 Hz, 1H, $CpCH_2N$); 4.07 (s, 5H, C_5H_5); 4.19 (m, 1H, RC_4H_2CH); 4.25 (m, 1H, RC_4H_2CH). – ^{13}C NMR ($CDCl_3$): δ = 0.23 ($SiCH_3$); 22.40 (NCH_2CH_2); 28.90 ($NCHCH_2CH_2$); 53.96 ($CpCH_2N$); 54.91 (NCH_2CH_2); 58.92 (OCH_3); 63.15 (NCH); 68.67 (C_5H_5); 69.19 (RC_4H_2CH); 71.56 ($RC_4H_3CCH_2N$); 73.77 (RC_4H_2CH); 74.36 (RC_4H_2CH); 76.89 (CH_2OCH_3); 90.29 (RC_4H_3CSi). – MS (70 eV), *m/z* (%): 385 (22)

[M^+], 271 (100) [M^+ − SMP], 199 (5) [$CpFeC_5H_4CH_2^+$]. − $C_{20}H_{31}FeNOSi$ (385.4): calcd. C 62.33, H 8.11, N 3.64; found C 62.51, H 8.34, N 3.53.

(S,R$_p$)-1-Diphenylphosphanyl-2-[(2-methoxymethylpyrrolidin-1-yl)methyl]-3-trimethylsilylferrocene (**4**): To **3** (620 mg, 1.61 mmol) in 10 ml of Et_2O at −78 °C was added 1.2 ml of 1.6 M *n*BuLi (1.94 mmol, 1.2 equiv.), the solution was stirred for 4 h, and warmed up to room temp. Ph_2PCl (428 mg, 1.94 mmol) was added at −78 °C and the mixture was worked up as described above for **2a**. Crude **4** (90% de) was purified by column chromatography on alumina with hexane/Et_2O (10:1) giving 750 mg (82%) of pure **4** as a red oil. {1,1′-Bis(diphenylphosphanyl)-2-[(2-methoxymethylpyrrolidin-1-yl)methyl]-3-trimethylsilylferrocene was eluted as a second band.} − de: 90%. − ^{1}H NMR ($CDCl_3$): δ = 0.24 (s, 9H, $SiCH_3$); 1.08−1.36 (m, 4H, $NCH_2CH_2CH_2$); 1.61 (m, 1H, NCH_2CH_2); 2.28 (m, 1H, NCH_2CH_2); 2.42 (m, 1H, NCH); 3.04 (d/d, ^2J = 9.2 Hz, ^3J = 6.5 Hz, 1H, CH_2OCH_3); 3.25 (s, 3H, OCH_3); 3.35 (d/d, ^2J = 9.2 Hz, ^3J = 5.5 Hz, 1H, CH_2OCH_3); 3.51 (d/d, ^2J = 12.5 Hz, $^4J_{H-P}$ = 4.0 Hz, 1H, $CpCH_2N$); 3.78 (s, 5H, C_5H_5); 3.94 (d, ^3J = 2.4 Hz, 1H, R_3C_4HCH); 4.05 (d, ^2J = 12.5 Hz, 1H, $CpCH_2N$); 4.14 (d, ^3J = 2.4 Hz, 1H, R_3C_4HCH); 7.15 (m, 5H, phenyl CH); 7.29 (m, 3H, phenyl CH); 7.52 (m, 2H, phenyl CH). − ^{13}C NMR ($CDCl_3$): δ = 0.87 ($SiCH_3$); 21.99 (NCH_2CH_2); 28.49 ($NCHCH_2CH_2$); 53.19 ($^3J_{C-P}$ = 12.1 Hz, $CpCH_2N$); 53.54 (NCH_2CH_2); 58.89 (OCH_3); 63.37 (NCH); 69.75 (C_5H_5); 73.04 (d, J_{C-P} = 4.9 Hz, R_3C_4HCH); 75.11 (d, J_{C-P} = 2.2 Hz, $R_2C_4H_2CCH_2$); 76.14 (R_3C_4HCH); 76.49 (CH_2OCH_3); 79.08 (d, J_{C-P} = 9.3 Hz, $R_2C_4H_2CSi$); 96.57 (d, J_{C-P} = 26.6 Hz, $R_2C_4H_2CP$); 127.58 (phenyl *p*-CH); 127.64 (d, J_{C-P} = 6.6 Hz, phenyl *o*-CH); 127.90 (d, J_{C-P} = 8.2 Hz, phenyl *o*-CH); 128.84 (phenyl *p*-CH); 132.71 (d, J_{C-P} = 18.6 Hz, phenyl *m*-CH); 135.18 (d, J_{C-P} = 22.0 Hz, phenyl *m*-CH), 138.46 (d, J_{C-P} = 9.3 Hz, phenyl CP); 139.85 (d, J_{C-P} = 8.2 Hz, phenyl CP). − ^{31}P NMR ($CDCl_3$): δ = −25.82. − MS (70 eV), *m/z* (%): 569 (57) [M^+], 538 (12) [$M^+ - OCH_3$], 456 (100) [$M^+ + H$ − SMP], 455 (94) [M^+ − SMP], 271 (21) [$CpFeC_5H_3(CH_2)(Si(CH_3)_3^+$]. − $C_{32}H_{40}FeNOPSi$ (569.6): calcd. C 67.48, H 7.08, N 2.46; found C 67.55, H 7.46, N 2.40.

(S,R$_p$)-1-Diphenylphosphanyl-2-[(2-methoxymethylppyrrolidin-1-yl)methyl]ferrocene (**2b**): To **4** (355 mg, 0.62 mmol) in 5 ml of DMSO was added 70 mg (0.63 mmol) of KO*t*Bu in 5 ml of DMSO at 0 °C and the solution was stirred at room temp. for 16 h; 20 ml of Et_2O and 15 ml of a concd. NaCl solution were added, the phases were separated and the aqueous phase was extracted with two 10-ml portions of Et_2O. The combined organic phases were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product (88% de) was filtered through alumina with hexane/Et_2O (4:1) and the filtrate was evaporated to dryness. Crystallization of the residue from hexane at −18 °C gave 181 mg of **2b** as red crystals. An additional 102 mg of **2b** was obtained from the mother liquor upon concentration and cooling to −18 °C. Total yield 283 mg (91%, de: >98%). − ^{1}H NMR ($CDCl_3$): δ= 1.36−1.51 (m, 3H, ring CH_2); 1.67 (m, 1H, ring CH_2); 2.00 (m, 1H, NCH_2CH_2); 2.58 (m, 1H, NCH); 2.69 (m, 1H, NCH_2CH_2); 3.11 (dd, ^2J = 9.5 Hz, ^3J = 6.7 Hz, 1H, OCH_2); 3.26 (d/d, ^2J = 9.5 Hz, ^3J = 4.6 Hz, 1H, OCH_2); 3.33 (s, 3H, OCH_3); 3.65 (d/d, ^2J = 13.4 Hz, $^4J_{P-C}$ = 2.1 Hz, 1H, $CpCH_2N$); 3.83 (m, 1H, $R_2C_4H_2CH$); 3.93 (d, ^2J = 13.4 Hz, 1H, $CpCH_2N$); 3.94 (s, 5H, C_5H_5); 4.28 (m, 1H, $R_2C_4H_2CH$); 4.57 (m, 1H, $R_2C_4H_2CH$); 7.22 (m, 5H, phenyl CH); 7.37 (m, 3H, phenyl CH); 7.58 (m, 2H, phenyl CH). − ^{13}C NMR ($CDCl_3$): δ = 22.91 (NCH_2CH_2); 28.34 ($NCHCH_2CH_2$); 53.10 (d, $^3J_{C-P}$ = 8.8 Hz, $CpCH_2N$); 54.42 (NCH_2CH_2); 58.95 (OCH_3); 62.72 (NCH); 69.34 (C_5H_5); 70.28 ($R_2C_4H_2CH$); 71.25 (d, J_{C-P} = 4.4 Hz, $R_2C_4H_2CH$); 72.68 (d, J_{C-P} = 3.9 Hz, $R_2C_4H_2CH$); 75.62 (d, J_{C-P} = 8.2 Hz, $RC_4H_3CCH_2$); 76.23 (CH_2OCH_3), 91.99 (d, J_{C-P} = 25.8 Hz, RC_4H_3CP); 127.71 (phenyl *p*-CH), 127.83 (d, J_{C-P} = 6.1 Hz, phenyl *o*-CH); 128.03 (d, J_{C-P} = 7.7 Hz, phenyl *o*-CH), 129.00 (phenyl *p*-CH), 132.63 (d, J_{C-P} = 18.1 Hz, phenyl *m*-CH); 135.19 (d, J_{C-P} = 21.4 Hz, phenyl *m*-CH); 138.06 (d, J_{C-P} = 8.3 Hz, RC_5H_3PC); 140.02 (d, J_{C-P} = 8.2 Hz, RC_5H_3PC). − ^{31}P NMR ($CDCl_3$): δ = −24.83. − $C_{29}H_{32}FeNOP$ (497.4): calcd. C 70.03, H 6.48, N 2.82; found C 70.19, H 6.77, N 2.83.

(S$_p$)-1-Diphenylphosphanyl-2-acetyloxymethylferrocene (**5**): **2a** (714 mg, 1.44 mmol) was heated at reflux in 10 ml of acetic anhydride for 10 h. After cooling to room temp. 30 ml of Et_2O was added, the mixture was washed with 2 M NaOH and a concd. NaCl solution, and dried with Na_2SO_4. Removal of the solvent in vacuo and crystallization of the residue from CH_2Cl_2/Et_2O gave 495 mg (79%) of **5** as small yellow crystals. − ^{1}H NMR ($CDCl_3$): δ = 1.58 (s, 3H, CH_3); 3.77 (m, 1H, $R_2C_4H_2CH$); 4.06 (s, 5H, C_5H_5); 4.30 (m, 1H, $R_2C_4H_2CH$); 4.52 (m, 1H, $R_2C_4H_2CH$); 4.98 (d, ^2J = 11.9 Hz, 1H, CH_2); 5.16 (d/d, ^2J = 11.9 Hz, J_{H-P} = 2.4 Hz, 1H, CH_2); 7.15−7.25 (m, 5H, phenyl CH); 7.35−7.38 (m, 3H, phenyl CH); 7.55−7.60 (m, 2H, phenyl CH). − ^{13}C NMR ($CDCl_3$): δ = 20.38 (CH_3); 61.81 (d, J_{C-P} = 9.9 Hz, CH_2); 69.65 (C_5H_5); 70.04 ($R_2C_4H_2CH$); 72.32 (d, J_{C-P} = 3.8 Hz, $R_2C_4H_2CH$); 73.07 (d, J_{C-P} = 3.9 Hz, $R_2C_4H_2CH$); 77.74 (d, J_{C-P} = 9.3 Hz, $RC_4H_3CCH_2$); 86.32 (d, J_{C-P} = 24.7 Hz, RC_4H_3CCP); 127.87 (phenyl *p*-CH); 127.96 (d, J_{C-P} = 6.6 Hz, phenyl *o*-CH); 128.24 (d, J_{C-P} = 7.7 Hz, phenyl *o*-CH); 129.23 (phenyl *p*-CH); 132.55 (d, J_{C-P} = 18.7 Hz; phenyl *m*-CH); 134.99 (d, J_{C-P} = 20.8 Hz, phenyl *m*-CH); 137.07 (d, J_{C-P} = 8.3 Hz, phenyl CP); 139.73 (d, J_{C-P} = 10.4 Hz, phenyl CP); 170.66 ($COCH_3$): − ^{31}P NMR ($CDCl_3$): δ = −23.69. − MS (70 eV), *m/z* (%): 458 (13) [M^+ + O], 393 (100) [458 − C_5H_5]. − $C_{25}H_{23}FeO_2P$ (442.3): calcd. C 67.89, H 5.24; found C 67.17, H 5.15.

(S$_p$)-1-Diphenylphosphanyl-2-(hydroxymethyl)ferrocene (**6**): To a solution of **5** (322 mg, 0.73 mmol) in 15 ml of MeOH and 5 ml of THF was added a solution of 1.5 g (27 mmol) of KOH in 10 ml of H_2O and the mixture was heated at reflux for 2 h. The solvent was evaporated in vacuo, the residue was treated with 15 ml of H_2O and extracted with three 15-ml portions of Et_2O. The combined organic phases were dried with Na_2SO_4 and the solvent was removed in vacuo. Crystallization of the residue from hexane gave 275 mg (94%) of **6** as orange crystals. − ^{1}H NMR ($CDCl_3$): δ = 1.41 (br. t, ^3J = 6.0 Hz, 1H, OH); 3.75 (m, 1H, $R_2C_4H_2CH$): 4.09 (s, 5H, C_5H_5); 4.30 (m, 1H, $R_2C_4H_2CH$); 4.41 (d/d, ^2J = 12.5 Hz, ^3J = 6.0 Hz, 1H, CH_2), 4.52 (m, 1H, $R_2C_4H_2CH$); 4.53 (d/d/d, ^2J = 12.5 Hz, ^3J = 6.0 Hz, J_{H-P} = 1.5 Hz, 1H, CH_2); 7.21 (m, 2H, phenyl CH); 7.26 (m, 3H, phenyl CH); 7.39 (m, 3H, phenyl CH); 7.52 (m, 2H, phenyl CH). − ^{13}C NMR ($CDCl_3$): δ = 59.97 (d, J_{C-P} = 8.8 Hz, CH_2); 69.48 (C_5H_5); 69.65 ($R_2C_4H_2CH$); 71.60 ($R_2C_4H_2CH$); 71.74 ($R_2C_4H_2CH$), 92.65 (d, J_{C-P} = 23.0 Hz, RC_4H_3CP); 128.3−128.4 (several signals, phenyl CH); 129.29 (phenyl *p*-CH); 132.44 (d, J_{C-P} = 18.1 Hz, phenyl *m*-CH); 134.85 (d, J_{C-P} = 20.3 Hz, phenyl *m*-CH); 136.86 (RC_5H_3PC); 139.74 (RC_5H_3PC). − ^{31}P NMR ($CDCl_3$): δ = −23.56. − MS (70 eV), *m/z* (%): 400 (22) [M^+], 384 (9), 279 (19), 149 (100). − $C_{23}H_{21}FeOP$ (400.2): calcd. 69.02, H 5.29; found C 68.91, H 5.31.

Allyl[(S,S$_p$)-1-Diphenylphosphanyl-2-[(2-methoxymethylpyrrolidin-1-yl)methyl]ferrocene-N,P]palladium(II) Hexafluorophosphate (**7**·PF_6): To a solution of **2a** (74.6 mg, 0.15 mmol) in 10 ml of EtOH was added 27.4 mg (0.075 mmol) of solid $[(C_3H_5)PdCl]_2$ in one portion and the mixture was stirred for 1 h at 40 °C. NH_4PF_6

(47 mg, 0.29 mmol) was added and stirring was continued for 3 h at room temp. during which time an orange solid precipitated which was isolated by filtration. Recrystallization of the solid from CH_2Cl_2/Et_2O gave 103 mg (87%) of pure **7**·PF_6. – ^1H NMR (CD_2Cl_2): δ = 1.80 (m, 2H, NCHCH_2 and $NCH_2CH_2CH_2$); 1.95 (m, 1H, NCH_2CH_2); 2.03 (m, 1H, CH_2CHCH_2), 2.16 (m, 1H, $NCHCH_2$); 2.58 (m, 1H, NCH_2CH_2); 3.06 (m, 2H, $NCH_2CH_2CH_2$ and NC*H*); 3.29 (m, 1H, CH_2CHCH_2); 3.37 (d, ^2J = 13.5 Hz, 1H, $CpCH_2N$); 3.50 (s, OCH_3); 3.62 (m, 1H, CH_2CHCH_2); 3.70 (s, C_5H_5); 3.71–3.82 (m, 2H, OCH_2); 4.44 (m, 1H, $R_2C_4H_2CH$); 4.51 (m, 1H, $R_2C_4H_2CH$); 4.67 (m, 1H, $R_2C_4H_2CH$); 4.76 (d, ^2J = 13.5 Hz, 1H, $CpCH_2N$); 4.97 (m, 1H, CH_2CHCH_2); 5.57 (m, 1H, CH_2CHCH_2); 7.22 (m, 2H, phenyl CH); 7.42 (m, 3H, phenyl CH); 7.72 (m, 3H, phenyl CH); 7.92 (m, 2H, phenyl CH). – ^{31}P NMR (CD_2Cl_2): δ = 18.08, –144.85 (sept, J_{F-P} = 711 Hz, PF_6). – ^{13}C NMR (CD_2Cl_2): δ = 22.29; 26.76; 57.41; 59.51; 60.67; 62.88; 70.50; 71.19; 73.41; 74.08; 75.99; 84.13; 87.65; 119.98; 129.34; 129.72; 130.74; 131.69; 132.96; 135.77. – MS (SIMS, 70 eV), *m/z* (%): 644 (0.6) [$M^+ - PF_6$], 604 (0.8) [644 – C_5H_5], 530 (100) [644 – SMP]. – $C_{32}H_{37}F_6FeNOP_2Pd$ (789.8): calcd. C 48.66, H 4.72, N 1.77; found C 48.69, H 4.50, N 1.70.

X-Ray Structural Analysis of **7**·PF_6: $C_{32}H_{37}F_6FeNOP_2Pd$, M = 789.84 g mol^{-1}, orthorhombic space group $P2_12_12_1$ (no. 19), a = 9.662(7), b = 16.707(4), c = 19.919(4) Å, V = 3215.0(4) Å^3, Z = 4, $d_{calcd.}$ = 1.632 g cm^{-3}, μ(Mo-K_α) 11.62 cm^{-1}, F(000) = 1600. ENRAF-Nonius CAD4, ω-scan, Mo-K_α radiation (0.71073 Å), graphite monochromator, 5407 reflections ($+h$, $+k$, $+l$) at 253 K with $3 \leq \theta \leq 28°$, crystal size 0.6 × 0.4 × 0.2 mm^3. Empirical absorption correction (PSI scans). Structure solution with Patterson methods. Refinement[16] with isotropic thermal parameters for hydrogen and anisotropic displacement parameters for the other atoms converged at R = 0.026, R_w = 0.034 for 397 parameters and 4724 independent observations with $I > 1.0\sigma(I)$. A final difference Fourier synthesis showed a residual density of 0.77/–0.39 eÅ^{-3}[17].

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