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Synthesis and Structure of Enantiomerically Pure Ferrocene Derivatives for Nonlinear Optics

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Summary: The synthesis of enantiomerically pure (S)-1-formyl-2-vinylferrocene (6) from (R)-N,N-dimethyl-(1-ferrocenylethyl)amine (1) is reported. 6 is the common precursor for the preparation, via Wittig methodology, of planar chiral conjugated donor–acceptor systems for nonlinear optics. The compounds (S)-1-(2-(4-nitrophenyl)-E-ethenyl)-2-vinylferrocene (7), (S)-1-(4-(4-nitrophenyl)-E,E-1,3-butadienyl)-2-vinylferrocene (8), and (S)-1-(6-(4-nitrophenyl)-E,E,E-1,3,5-hexatrienyl)-2-vinylferrocene (9) were characterized by X-ray diffraction. Crystals of 7 and 8 are orthorhombic, space group $P2_12_12_1$. *7:* $a = 8.242(1)$ Å, $b = 10.236(3)$ Å, $c = 38.863(5)$ Å, $V = 3278(2)$ Å^3, $Z = 8$ *(two symmetry-independent molecules per unit cell). 8:* $a = 6.881(1)$ Å, $b = 9.036(1)$ Å, $c = 30.159(3)$ Å, $V = 1875.2(5)$ Å^3, $Z = 4$. *Crystals of 9 are monoclinic, space group* $P2_1$, *with* $a = 8.335(1)$ Å, $b = 7.540(1)$ Å, $c = 16.042(2)$ Å, $\beta = 97.21(1)°$, $V = 1000.2(4)$ Å^3, *and* $Z = 2$. *All three compounds show a pairwise antiparallel arrangement of the molecules in the solid state.*

The report by Green et al. in 1987 on the nonlinear optical properties of *cis*-[1-ferrocenyl-2-(4-nitrophenyl)-ethylene], exhibiting a large SHG (second harmonic generation) efficiency, constituted a breakthrough.[1] Since then, organometallic compounds consisting of conjugated donor–acceptor systems have attracted increasing attention.[2] This resulted in the development of other ferrocene derivatives with even larger SHG efficiencies.[3] For this purpose the NLO material needs to crystallize in a noncentrosymmetric space group.[4] This prerequisite is usually achieved by pursuing a trial-and-error strategy, i.e., practically by a systematic variation of substituents, ligands, and/or counterions.[5] Considering that the absence of inversion symmetry is by definition a property of chiral, enantiomerically pure compounds, it is somewhat surprising to note that there is only one report in the literature concerning the utilization of optically enriched, planar chiral ferrocene derivatives.[6] On the other hand, chiral organic materials, i.e., derivatives of carbohydrates, amino acids, terpenoids, etc. have been utilized quite often.[7] However, one observes that chirality is just one possible strategy for obtaining enantiomorphous space groups and that optimum dipolar alignment is determined by a complex combination of electronic and steric factors.[7]

Results and Discussion

We report herein the synthesis and structure of the first enantiomerically pure ferrocene derivatives with potential NLO properties. The key intermediate is (*S*)-1-formyl-2-vinylferrocene (6). Its synthesis is achieved in five steps from the well-known (*R*)-*N*,*N*-dimethyl(1-ferrocenylethyl)amine (1), readily available in optically pure form.[8] The synthetic sequence is shown in Scheme I.

The known hydroxymethyl derivative 2[8a] was prepared via lithiation of 1,[8a] followed by reaction with CO_2 in diethyl ether, and reduction of the raw intermediate carboxylate with $LiAlH_4$ in THF. This procedure gives slightly higher yields (60% after recrystallization) than the previously reported direct hydroxymethylation of the lithium derivative with gaseous formaldehyde.[8a] After protection of the hydroxyl function with TBDMSCl/NEt_3, formal elimination of dimethylamine was achieved cleanly by treatment with 0.5 equiv of trichloromethyl chloroformate (diphosgene).[9] Deprotection of the silyl ether 4 with $[NBu_4]F$ in THF gave (*S*)-1-(hydroxymethyl)-2-vinylferrocene (5) in excellent yields. Oxidation of 5 with MnO_2 in CH_2Cl_2 (or $CHCl_3$/petrolether, 1:1 volume) afforded the aldehyde (*S*)-6 as a brown viscous oil. Because of relatively rapid decomposition reactions, 6 could not be stored for prolonged periods of time and had to be used immediately.

Starting from the freshly prepared aldehyde 6, three conjugated nitrophenyl derivatives (7–9) were synthesized by utilizing the corresponding Wittig reagents,[10] as shown in Scheme II.

We found that triethylphosphoranes, generated in situ from the corresponding phosphonium salts by deproto-

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(2) For a review, see: Nalwa, H. S. *Appl. Organomet. Chem.* **1991**, *5*, 349–377.

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(4) For a general discussion, see: (a) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991. (b) Marder, S. R., Sohn, J. E., Stucky, G. D., Eds. *Materials for Nonlinear Optics. Chemical Perspectives*; ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991.

(5) For a discussion of the inter-relationships between molecular, crystal structural, and optical properties of NLO materials, see: Bailey, H. E.; Cruickshank, F. R.; Pavlides, P.; Pugh, D.; Sherwood, J. N. *J. Phys. D: Appl. Phys.* **1991**, *24*, 135–144.

(6) Bunting, H. E.; Green, M. L. H.; Marder, S. R.; Thompson, M. E.; Bloor, D.; Kolinsky, P. V.; Jones, R. J. *Polyhedron* **1992**, *11*, 1489–1499.

(7) To this subject, see the comprehensive review: Nicoud, J. F.; Twieg, R. J. In *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: Orlando, FL, 1987; Vol. 1, pp 227–296.

(8) (a) Marquarding, D.; Klusacek, H.; Gokel, G. W.; Hoffmann, P.; Ugi, I. *J. Am. Chem. Soc.* **1970**, *92*, 5389–5393. (b) Gokel, G.; Ugi, I. *J. Chem. Educ.* **1972**, *49*, 294–296.

(9) A similar reaction utilizing phosgene has previously been reported: Marquarding, D.; Burghard, H.; Ugi, I.; Urban, R.; Klusacek, H. *J. Chem. Res. S* **1977**, 82–83; *J. Chem. Res. M* **1977**, 915–958.

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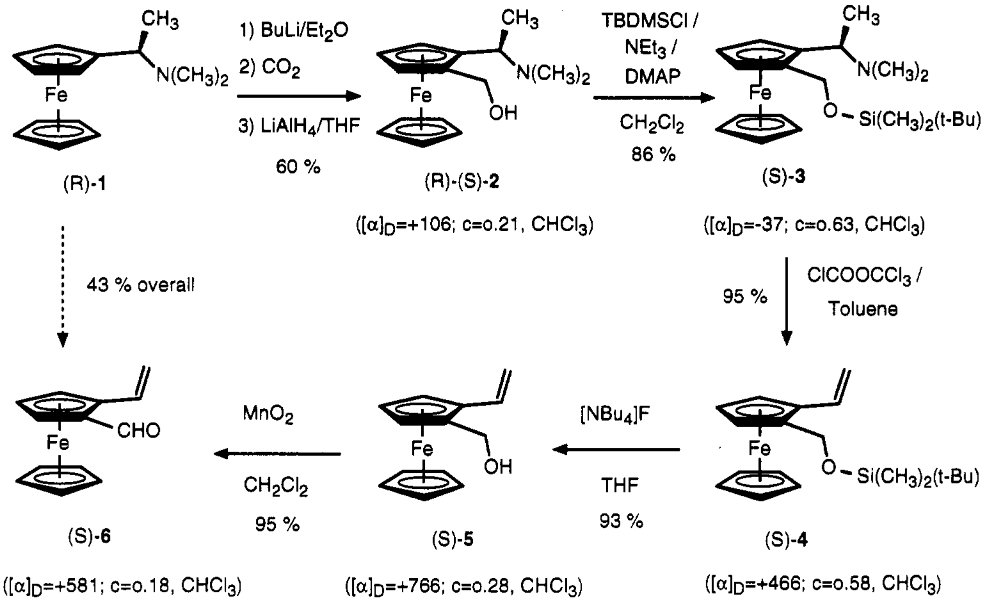
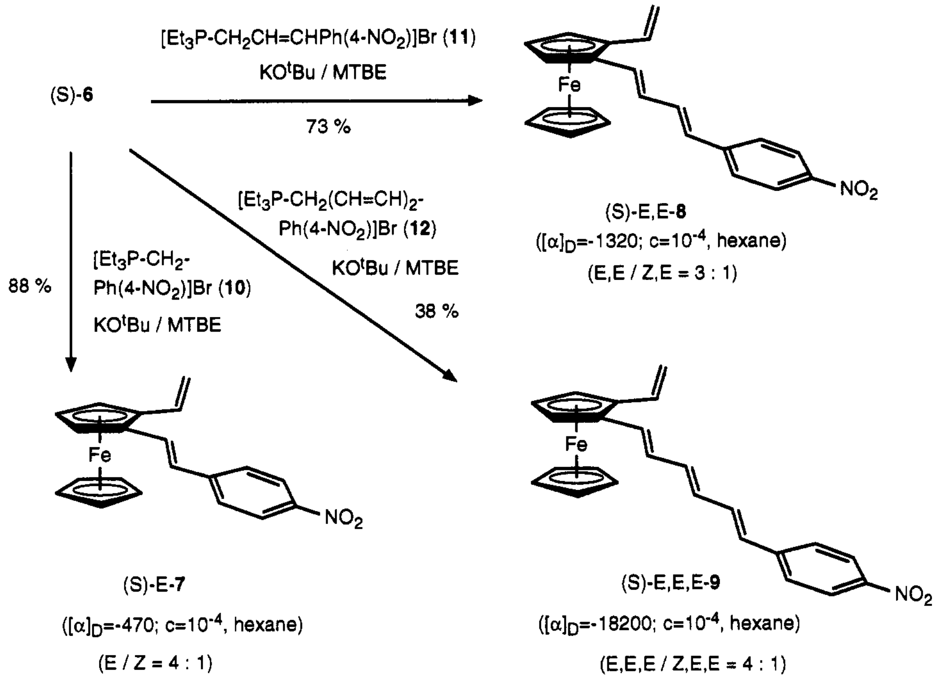
Scheme I



Scheme II



nation with KO^{t}Bu in MTBE, gave superior results with regards to olefin geometry. Whereas such aliphatic phosphoranes afforded 3-4:1 mixtures of *E* and *Z* isomers, reagents derived from triphenylphosphine gave poorer cis/trans ratios (ca. 1:1). In all three cases, stereoisomerically pure compounds could be obtained by column chromatography. The products **7**–**9** were then recrystallized from ethyl acetate and isolated in form of deep purple platelets. The *Z*-, *Z,E*-, and *Z,E,E*-isomers, respectively, could not be induced to crystallize and were isolated as dark red oils.

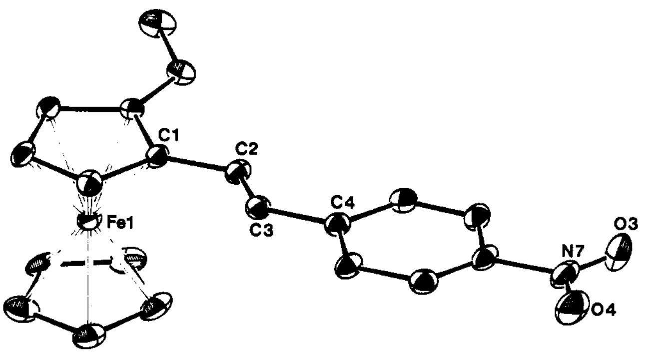


Figure 1. ORTEP view of one of the two symmetry-independent molecules of **7**. Selected bond lengths (in Å) are C1–C2 = 1.436(8), C2–C3 = 1.367(8), and C3–C4 = 1.506(7).

An X-ray crystallographic study for each of the three compounds was carried out. Crystal data and details of refinement are given in Table I, whereas Figures 1–3 show views of the molecules.

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(10) The allyltriethylphosphonium bromide salts needed (**10**–**12**) were prepared by reacting the corresponding allyl bromides with a slight excess of PEt$_3$ in boiling benzene or toluene. The allyl bromides were obtained by conventional synthetic methodologies; see, e.g.: (a) Drew, J.; Letellier, M.; Morand, P.; Szabo, A. G. *J. Org. Chem.* **1987**, *52*, 4047–4052. (b) Huang, Y.; Shen, Y.; Zheng, J.; Zhang, S. *Synthesis* **1985**, 57–58.

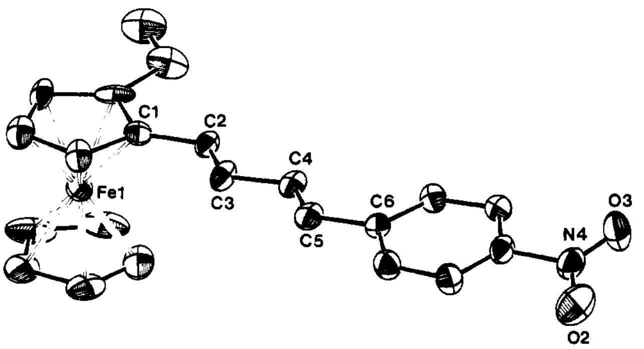

Figure 2. ORTEP view of **8**. Selected bond lengths (in Å) are C1–C2 = 1.472(5), C2–C3 = 1.332(5), C3–C4 = 1.452(6), C4–C5 = 1.339(5), and C5–C6 = 1.478(5).

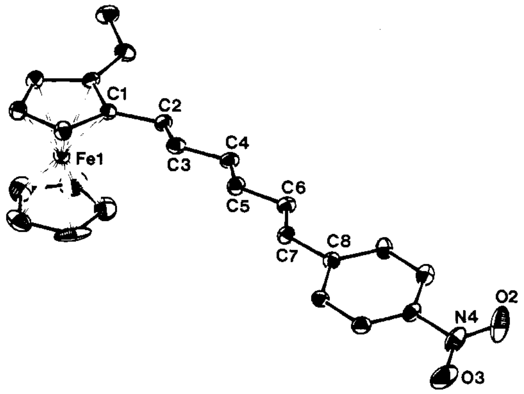

Figure 3. ORTEP view of **9**. Selected bond lengths (in Å) are C1–C2 = 1.429(5), C2–C3 = 1.439(6), C3–C4 = 1.472(5), C4–C5 = 1.332(5), C5–C6 = 1.452(6), C6–C7 = 1.339(5), and C7–C8 = 1.478(5).

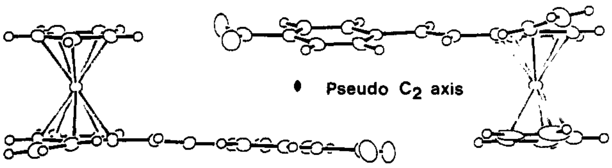

Figure 4. Pairwise antiparallel arrangement of the molecules in **7**, via pseudo C_2 symmetry.

For all three structures bonding parameters fall in the expected range.[11,12] Several overall structural features, common to **7**–**9**, are worth mentioning. The two conjugated substituents in each of the three different complexes are found to only slightly deviate from coplanarity with the respective cyclopentadienyl ring. As expected, the vinyl group points away from the larger substituent, thus being approximately aligned with its double bond(s).

Compound **7** crystallizes in the orthorhombic space group $P2_12_12_1$, with two independent molecules in the asymmetric unit. No significant differences in bonding parameters between these two molecules were found. The most interesting and, in view of the NLO properties, the most decisive feature revealed by the crystal structure is the relative position of these two molecules. As illustrated in Figure 4, they are related by a pseudo C_2 symmetry axis. The unit cell thus contains four pairs of molecules in almost perfect antiparallel arrangement. A similar, albeit less clearly defined situation, is found for the compounds **8** and **9**. Derivative **8** which crystallizes in the same space group as **7**, but with only one symmetry-independent molecule in the unit cell, also shows a pairwise antiparallel orientation of the molecules. The same is true for the trienyl derivative **9** in the monoclinic space group $P2_1$.

On the basis of these structural features, it is not expected that the compounds **7**–**9** will exhibit large SHG efficiencies. It can be speculated that the pseudo C_2 symmetry relating the two independent molecules in the crystals of derivative **7** possibly corresponds to an inversion symmetry for the related achiral (2-(4-nitrophenyl)-*E*-ethenyl)ferrocene. Although its crystal structure has not been reported, it is known that this compound displays an SHG efficiency of 0.[1]

In summary, we offer a method for preparing enantiomerically pure organometallic compounds for applications in nonlinear optics. In our planar chiral 1,2-difunctionalized ferrocenes the vinyl group is not only a spectator substituent. One can imagine that it could be used for the incorporation of these molecules into, e.g., polymeric structures or structures homologated with a long hydrocarbon chain for the preparation of Langmuir–Blodgett films.[13]

Experimental Section

General Considerations. All reactions with air- or moisture-sensitive materials were carried out under Ar using standard Schlenk techniques. Freshly distilled, dry, and oxygen-free solvents were used throughout. Routine ^{1}H NMR spectra (250.133 MHz) were recorded with a Bruker AC 250 spectrometer. Chemical shifts are given in ppm relative to internal TMS and coupling constants (*J*) are given in Hz. Optical rotations were measured with a Perkin-Elmer 241 polarimeter using 10-cm cells. Melting points were measured in open capillaries with a Büchi-510 apparatus and are uncorrected. Low-resolution EI/MS spectra were recorded at 70 eV on a Finnigan MAT 212/SS300 spectrometer. Merck silica gel 60 (70–230 mesh) was used for flash column chromatography. Thin-layer chromatography (TLC) was performed with Merck silica gel 60 F254 precoated glass plates. Elemental analyses were performed by Analytical Research Services, Ciba-Geigy AG.

***N,N*-Dimethyl-[(*R*)-1-[(*S*)-2-(hydroxymethyl)ferrocenyl]-ethyl]amine (2).** To a solution of 10 g (38.9 mmol) of *N,N*-dimethyl-(*R*)-(1-ferrocenylethyl)amine (**1**) in 60 mL of diethyl ether was added 36.5 mL of a 1.6 M solution of BuLi in hexane (58.4 mmol), and the mixture was stirred over night at room temperature. The solution of the metalated derivative was then added via canula to a stirred suspension of dry ice (excess) in 40 mL of Et_2O. A yellow, finely divided precipitate immediately formed. After consumption of the CO_2, the mixture was stirred at room temperature for 1 h. Thereafter, the precipitate was filtered off, washed with Et_2O and petroleum ether, and dried in vacuo during 2 h. The raw lithium ferrocenecarboxylate (9.6 g) was redissolved in 50 mL of THF and added dropwise to a solution of 3.75 g (98.9 mmol) of $LiAlH_4$ in 100 mL of THF. After being refluxed over night, the mixture was cooled to 0 °C and diluted with 100 mL of Et_2O. Hydrolysis was carried out by careful addition of 15 mL of H_2O and 15 mL of a 15% NaOH solution, successively. The mixture was then stirred at room temperature for 0.5 h, and the white, solid residue was filtered

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(11) For a compilation of bond distances of organic, organometallic, and coordination compounds, see: (a) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans.* 2 **1987**, supplement S1–S19. (b) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, supplement S1–S83.

(12) The crystallographic data (atomic coordinates and bonding parameters) have been placed in the supplementary material. This is because the main goals of the X-ray diffraction studies were to (a) confirm the structure of compounds **7**–**9** and (b) clarify the relative orientation of the molecules in the unit cell. Further, the molecular structures do not present any exceptional features.

(13) For this subject see, e.g., ref 4a, pp 152–171.

off and washed with Et_2O. The combined filtrates were dried over Na_2SO_4 and evaporated in vacuo, giving an orange, solid material. (Occasionally the crude product was also obtained as an oil, which could not be induced to crystallize. In such cases purification was achieved by flash column chromatography. Eluent: EtOAc/hexane, 2:1 volume, containing 2 vol % NEt_3.) Recrystallization from hot cyclohexane gave 6.70 g (60%) of the desired product: $[\alpha]^{22}_D = +106.2$ ($CHCl_3$, $c = 0.210$); ^1H NMR ($CDCl_3$) δ 1.16 (d, $J = 7$, 3H), 2.04 (s, 6H), 3.91 (s, 5H), 3.90–4.05 (m, 4H), 4.09 (m, 1H), 4.67 (d, $J = 12$, 1H); MS m/z 287 (M^+), 242 (100%), 225, 213, 199, 134, 105. Anal. Calcd for $C_{15}H_{21}FeNO$: C, 62.74; H, 7.37; N, 4.88. Found: C, 62.83; H, 7.39; N, 4.83.

***N,N*-Dimethyl-[(*R*)-1-[(*S*)-2-((*tert*-butyldimethylsiloxy)methyl)ferrocenyl]ethyl]amine (3).** A 1.19-g amount (4.14 mmol) of **2** was dissolved in a CH_2Cl_2 solution (40 mL) containing 0.69 mL (5 mmol) of NEt_3 and 20 mg (0.17 mmol) of DMAP. A 0.69-g amount (4.56 mmol) of TBDMSCl, dissolved in 15 mL of CH_2Cl_2, was added dropwise, and the mixture was stirred over night at room temperature. After treatment with 15 mL of H_2O, the mixture was successively washed with 100-mL portions of saturated NH_4Cl, $NaHCO_3$, and NaCl solutions. The organic phase was then dried over Na_2SO_4, filtered, and evaporated in vacuo, leaving an oily residue. Chromatography (eluent: EtOAc/hexane, 1:4 volume, containing 2 vol % of NEt_3) gave 1.43 g (86%) of the pure title compound as an orange, viscous oil: $[\alpha]^{22}_D = -36.5$ ($CHCl_3$, $c = 0.63$); TLC (hexane/EtOAc, 3:1 volume, containing 1 vol % NEt_3) R_f 0.13; ^1H NMR δ –0.01 (s, 3H), 0.01 (s, 3H), 0.83 (s, 9H), 1.34 (d, $J = 7$, 3H), 1.97 (s, 6H), 3.55 (q, $J = 7$, 1H), 3.97 (m overlapping with s, 7H), 4.11 (t, $J = 2$, 1H), 4.27–4.38 (AB q, 2H); MS m/z 401 (M^+), 356 (100%), 225, 195, 134, 121, 105. Anal. Calcd for $C_{21}H_{35}FeNOSi$: C, 62.83; H, 8.79; N, 3.49. Found: C, 62.69; H, 8.73; N, 3.63.

(*S*)-1-((*tert*-Butyldimethylsiloxy)methyl)-2-vinylferrocene (4). To a toluene solution (20 mL) containing 2.9 g (7.2 mmol) of **3** and 1.17 mL of NEt_3 (8.4 mmol) was added dropwise 0.434 mL (3.6 mmol) of trichloromethyl chloroformate ("diphosgene"). The solution, already warmed to ca. 40 °C by the exothermic reaction taking place, was briefly (5 min) heated to reflux temperature, cooled, and treated with 3 × 50 mL portions of a saturated $NaHCO_3$ solution. After it had been washed with H_2O and brine, and dried over Na_2SO_4, the organic phase was evaporated in vacuo leaving an oily residue (ca. 100% yield). By ^1H NMR this material resulted to be of sufficient purity for further reactions. An analytical sample was obtained after purification by flash chromatography (eluent: EtOAc/hexane, 1:30 volume) and drying in vacuo: $[\alpha]^{22}_D = +465.9$ ($CHCl_3$, $c = 0.58$); TLC (hexane/EtOAc, 30:1 volume) R_f 0.56; ^1H NMR ($CDCl_3$) δ –0.03 (s, 3H), 0.00 (s, 3H), 0.83 (s, 9H), 3.98 (s, 5H), 4.08 (t, $J = 2.5$, 1H), 4.19 (m, 1H), 4.35 (m, 1H), 4.40–4.58 (AB q, $J = 12$, 2H), 5.01 (dd, $J = 11, 2$, 1H), 5.34 (dd, $J = 17.5, 2$, 1H), 6.50 (dd, $J = 17.5, 11$, 1H); MS m/z 356 (M^+, 100%), 299, 225, 195, 121. Anal. Calcd for $C_{19}H_{28}FeOSi$: C, 64.04; H, 7.92. Found: C, 63.68; H, 7.86.

(*S*)-1-(Hydroxymethyl)-2-vinylferrocene (5). A 2.4 g amount (6.7 mmol) of compound **4** in 200 mL of THF was treated with 16.75 mL of a 1 M solution of Bu_4NF in THF overnight at room temperature. To the clear mixture was then added 100 mL of H_2O, which was extracted with Et_2O (3 × 200 mL). The collected organic phases were washed with brine, dried over $MgSO_4$, and evaporated to dryness. The oily residue was purified by flash chromatography (eluent: EtOAc/hexane, 1:2 volume), giving 1.51 g (93%) of the title compound as an orange-brown, viscous oil: $[\alpha]^{22}_D = +765.5$ ($CHCl_3$, $c = 0.275$); TLC (hexane/EtOAc, 3:1 volume) R_f 0.36; ^1H NMR ($CDCl_3$) δ 4.11 (s, 5H), 4.24 (t, $J = 2.5$, 1H), 4.32 (m, 1H), 4.41–4.56 (AB q, $J = 12$, 2H), 4.51 (m, overlapping with previous q, 1H), 5.13 (dd, $J = 11, 1.5$, 1H), 5.44 (dd, $J = 17.5, 1.5$ 1H), 6.59 (dd, $J = 17.5, 11$, 1H); MS m/z 242 (M^+, 100%), 224, 213, 199, 159, 138, 121, 104. Anal. Calcd for $C_{13}H_{14}FeO$: C, 64.50; H, 5.83. Found: C, 64.74; H, 6.13.

(*S*)-1-Formyl-2-vinylferrocene (6). A 520-mg amount (2.15 mmol) of the hydroxymethyl derivative **5** in 14 mL of a 1:1 mixture of $CHCl_3$ and petroleum ether was treated with an excess of activated MnO_2 (2.71 g, 31.2 mmol) at room temperature. The reaction was monitored by TLC, and after 2.5 h no starting material was detectable. The insoluble inorganic reagent was filtered off, and the filtrate was evaporated in vacuo leaving a brown, oily residue. This was dissolved in Et_2O, and the solution was washed with H_2O, dried over $MgSO_4$, and evaporated. The crude product was purified by flash chromatography (eluent: EtOAc/hexane, 1:4 volume) giving 1.41 g (95%) of the ferrocenyl aldehyde as a brown, viscous oil: $[\alpha]^{22}_D = +581.3$ ($CHCl_3$, $c = 0.176$); TLC (hexane/EtOAc, 3:1 volume) R_f 0.63; ^1H NMR ($CDCl_3$) δ 4.13 (s, 5H), 4.55 (t, $J = 2.5$, 1H), 4.74 (m, 1H), 4.80 (m, 1H), 5.16 (dd, $J = 12, 1.5$, 1H), 5.44 (dd, $J = 17.5, 1.5$, 1H), 6.87 (dd, $J = 17.5, 12$, 1H), 10.06 (s, 1H); MS m/z 240 (M^+, 100%), 212, 210, 186, 184, 146, 134, 121. The compound was found to be rather unstable in undiluted form, and no consistent elemental analysis could be obtained.

(*S*)-1-(2-(4-Nitrophenyl)-*E*-ethenyl)-2-vinylferrocene (7). A 538 mg amount (1.59 mmol) of (4-nitrobenzyl)triethylphosphonium bromide (**10**) was treated with an equimolar amount of freshly sublimed KO^tBu (178 mg) in 60 mL of MTBE at room temperature. To the deep red solution of the immediately formed phosphorane was added a MTBE solution (10 mL) of the crude aldehyde **6**, which was prepared by MnO_2 oxidation of 232 mg (0.96 mmol) of the hydroxymethyl derivative **5**, as described above. The resulting mixture was then refluxed for 2 h. After cooling of the mixture to room temperature, 10 mL of a 10% solution of $NaHSO_3$ and 50 mL of H_2O were added, and the crude product was extracted with Et_2O (3 × 100 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The dark red solid residue (440 mg), which was shown by ^1H NMR to contain a ca. 4:1 mixture of the *E* and *Z* isomers of the product, was flash chromatographed (eluent: EtOAc/hexane, 1:40 volume), giving 201 mg of the title compound as crystalline material and 50 mg of its *Z* isomer as a viscous oil. Total yield: 73%. *E*-isomer: $[\alpha]^{22}_D = -470$ (hexane, $c = 0.0001$); mp 179–181 °C dec; TLC (hexane/EtOAc, 9:1 volume) R_f 0.56; ^1H NMR ($CDCl_3$) δ 4.12 (s, 5H), 4.47 (t, $J = 2.5$, 1H), 4.66–4.72 (m, 2H), 5.22 (dd, $J = 11.5, 1.5$, 1H), 5.48 (dd, $J = 17.5, 1.5$, 1H), 6.73 (dd, $J = 17.5, 11.5$ 1H), 6.78 (d, $J = 16.5$, 1H), 7.28 (d, $J = 16.5$, 1H), 7.57 and 8.20 (AA′BB′ system, 4H); MS m/z 359 (M^+, 100%), 313, 263, 191, 189, 165, 121. Anal. Calcd for $C_{20}H_{17}FeNO_2$: C, 66.88; H, 4.77; N, 3.90. Found: C, 67.01; H, 4.94; N, 4.02. *Z*-isomer: TLC (hexane/EtOAc, 9:1 volume) R_f 0.63; ^1H NMR ($CDCl_3$) δ 4.07 (s, 5H), 4.09 (m, partially overlapping with previous s, 1H), 4.25 (t, $J = 2.5$, 1H), 4.60 (m, 1H), 5.08 (dd, $J = 11, 1.5$, 1H), 5.40 (dd, $J = 17.5, 1.5$, 1H), 6.52 (d, $J = 12$, 1H), 6.54 (dd, $J = 17.5, 11$, 1H), 6.79 (d, $J = 12$, 1H), 7.42 and 8.08 (AA′BB′ system, 4H).

(*S*)-1-(4-(4-Nitrophenyl)-*E,E*-1,3-butadienyl)-2-vinylferrocene (8). This compound was prepared in an analogous manner as described for **7**. Starting from 432 mg (1.2 mmol) of (3-(4-nitrophenyl)-prop-2-*E*-enyl)triethylphosphonium bromide (**11**), 140 mg (1.25 mmol) of KO^tBu, and 240 mg (1 mmol) of vinyl alcohol **5**, 340 mg (88%) of a ca. 3:1 mixture (by ^1H NMR) of *E,E* and *Z,E* isomers was obtained. Column chromatography (eluent: EtOAc/hexane, 1:40 volume) gave the pure isomers. *E,E*-isomer: $[\alpha]^{22}_D = -1320$ (hexane, $c = 0.0001$); mp 130–135 °C dec; TLC (hexane/EtOAc, 9:1 volume) R_f 0.41; ^1H NMR ($CDCl_3$) δ 4.08 (s, 5H), 4.41 (t, $J = 2.5$, 1H), 4.59–4.67 (m, 2H), 5.19 (dd, $J = 11, 1.5$, 1H), 5.46 (dd, $J = 17, 1.5$, 1H), 6.55–6.85 (m, 4H), 7.06 (dd, $J = 17, 11$, 1H), 7.03 and 8.19 (AA′BB′ system, 4H); MS m/z 385 (M^+, 100%), 273, 236, 217, 215, 202, 189, 121. Anal. Calcd for $C_{22}H_{19}FeNO_2$: C, 68.59; H, 4.97; N, 3.64. Found: C, 68.28; H, 4.90; N, 3.68. *Z,E*-isomer: oil; TLC (hexane/EtOAc, 9:1 vol) R_f 0.46; ^1H NMR ($CDCl_3$) δ 4.12 (s, 1H), 4.46 (t, $J = 2.5$, 1H), 4.57 (m, 1H), 4.64 (m, 1H), 5.16 (dd, $J = 10.5, 1.5$, 1H), 5.45 (dd, $J = 17, 1.5$, 1H), 6.36 (t, $J = 11$, 1H), 6.48 (m, 1H), 6.55–6.70 (m, 3H), 7.36 (m, 1H), 7.48 and 8.15 (AA′BB′ system, 4H).

(*S*)-1-(6-(4-Nitrophenyl)-*E,E,E*-1,3,5-hexatrienyl)-2-vinylferrocene (9). This compound was prepared in an analogous manner as described for **7**. Starting from 386 mg (1 mmol) of

Table I. Summary of Crystal Data, Collection Data, and Refinement of 7–9

	compd		
	7	8	9
formula	$C_{20}H_{17}NO_2Fe$	$C_{22}H_{19}NO_2Fe$	$C_{24}H_{21}NO_2Fe$
mol wt	359.21	385.24	411.28
cryst system	orthorhombic	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
a(Å)	8.242(1)	6.881(1)	8.335(1)
b(Å)	10.236(3)	9.036(1)	7.540(1)
c(Å)	38.863(5)	30.159(3)	16.042(2)
β(deg)			97.21(1)
V(Å^3)	3278(2)	1875.2(5)	1000.2(4)
Z	8	4	2
D_{calc} (g·cm^{-3})	1.455	1.364	1.366
cryst size (mm)	0.50 × 0.10 × 0.07	0.58 × 0.48 × 0.04	0.50 × 0.33 × 0.03
diffractometer	Enraf-Nonius CAD4	Philips PW1100	Philips PW1100
radiation (graphite monochromated)	Cu Kα	Mo Kα	Mo Kα
wavelength (Å)	1.5418	0.7107	0.7107
scan mode	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
μ (cm^{-1})	74.9	8.161	7.70
F(000)	1488	800	428
scan range (2θ)	6–150	6–60	6–60
abs corr	empirical	none	none
transm factors	1.00/0.91		
no. of unique reflcns	3878	3978	3238
no. of obsd reflcns ($I > 3\sigma(I)$)	3744	1430	1395
refinement method	full matrix	full matrix	full matrix
no. of params	433	292	336
R	0.063	0.042	0.030
R_w	0.069	0.045	0.032
max/min density in final diff map (e Å^{-3})	0.724/–0.598	0.165/–0.173	0.238/–0.221

(5-(4-nitrophenyl)-penta-2,4-*E,E*-dienyl)triethylphosphonium bromide (**12**), 118 mg (1.05 mmol) of KO^{t}Bu, and 240 mg (1 mmol) of vinyl alcohol **5**, 156 mg (38%) of a ca. 4:1 mixture (by ^{1}H NMR) of *E,E,E*- and *Z,E,E*-isomers was obtained. Column chromatography (eluent: EtOAc/hexane, 1:40 volume) gave the pure *E,E,E*-isomer: $[\alpha]^{22}_D$ = –18200 (hexane, *c* = 0.0001); mp 175–180 °C dec; TLC (hexane/EtOAc, 9:1 volume) R_f 0.50; ^{1}H NMR ($CDCl_3$) δ 3.99 (s, 5H), 4.33 (t, *J* = 2.5, 1H), 4.52 (m, 1H), 4.56 (m, 1H), 5.60 (dd, *J* = 11, 1.5, 1H), 5.27 (dd, *J* = 17, 1.5, 1H), 6.36–6.67 (complex m, 6H), 6.95 (dd, *J* = 17, 11, 1H), 7.45 and 8.12 (AA′BB′ system, 4H); MS *m/z* 411 (M$^+$, 100%), 409, 299, 228, 212, 153, 121. Anal. Calcd for $C_{24}H_{21}FeNO_2$: C, 70.09; H, 5.15; N, 3.41. Found: C, 70.50; H, 5.47; N, 3.47. The *Z,E,E*-isomer could not be obtained in pure form. TLC (hexane/EtOAc, 9:1 volume) R_f 0.56.

X-ray Crystallographic Study of 7–9. Crystals suitable for X-ray diffraction of the compounds **7–9** were grown from diluted EtOAc solutions at room temperature. The crystals were glued to the tip of a Mark glass fiber using Araldit Rapid and covered with a thin film of the same glue. Intensity data were reduced by routine procedures. All calculations were performed on a Micro-Vax II computer using the commercial package SDP DIRDIF. The structures were solved by Patterson methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms could be localized for compounds **8** and **9**. Because for compound **7** only 20 hydrogen atoms (of 34) could be localized, these were inserted at calculated positions. Further details are given in Table I.

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Supplementary Material Available: For compounds **7–9**, figures showing atom-numbering schemes and packing diagrams and tables of atomic coordinates, displacement parameters, and bond distances and angles (27 pages). Ordering information is given on any current masthead page. Tables of observed and calculated structure factors (127 pages) are available from the authors upon request.

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