Cyclopentadienyl-Substituted Phosphaferrocenes: Synthesis of a Bis(phosphaferrocene) P,P-Chelate Ligand

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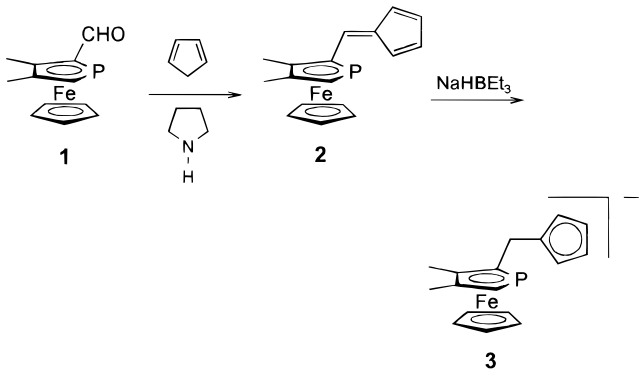
*Summary: The novel bis(phosphaferrocene)-substituted ferrocene **4** has been prepared from the corresponding cyclopentadienide **3** and shown to act as a P,P-chelate ligand in the Mo(CO)$_4$ complex **5**, which was structurally characterized. Enantiomerically pure (S,S)-**4** was used as ligand in the catalytic asymmetric allylic substitution.*

Introduction. Donor-functionalized cyclopentadienyl ligands have attracted considerable attention for various reasons. On one hand, they are capable of forming half-sandwich compounds, in which the intramolecular donor function coordinates to the central metal, sometimes in a hemilabile manner.[1] On the other hand, donor-functionalized Cp ligands may be used to assemble metallocene structures which can act as chelate ligands toward a metal fragment by virtue of their additional donor functions. This approach has been successfully followed in the case of ferrocenes as well as with several bent-metallocene systems.[2] In an extension of our previous work on the use of phosphaferrocene moieties as parts of P,P- or P,N-chelate ligand systems,[3] we now report on the synthesis of a phosphaferrocene-substituted cyclopentadienyl ligand and its first application in the formation of the corresponding ferrocene, thus giving straightforward access to a chiral bis(phosphaferrocene) P,P-chelate ligand.

Results and Discussion. Starting from the formylphosphaferrocene **1**, which is our standard building block for ligand preparation, we studied the introduction of a cyclopentadienyl group first by addition of LiCp, yielding the corresponding alcohol, which in turn could be reduced to the cyclopentadienylmethyl compound. However, the condensation of aldehyde **1** with cyclopentadiene in methanol in the presence of pyrrolidine turned out to be a superior method,[4] leading to the fulvene **2** in 95% yield.[5] The fulvene was converted to the cyclopentadienide **3** by hydride addition using 1.5 equiv of $NaBHEt_3$.[6] The cyclopentadienide precipitates as the sodium salt from hexane and can be stored under nitrogen after filtration.



The first complexation reaction carried out with the new ligand was the formation of the ferrocene **4** by treatment of 2 equiv of the anion **3** with 1 equiv of $FeCl_2$ in THF.[7] The reaction proceeded smoothly, and the ferrocene was isolated in 87% yield. When the racemic aldehyde *rac*-**1** is used as the starting material, two diastereomeric ferrocenes **4** are conceivable: the combination of both an *R*- and an *S*-configured phosphaferrocenyl cyclopentadienide to the ferrocene sandwich leads to an achiral C_s-symmetric *meso* form, whereas the combination of two homochiral phosphaferrocene building blocks, (*R*)- or (*S*)-**3**, leads to a pair of C_2-

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(2) For ferrocenes see: (a) Togni, A.; Hayashi, T. *Ferrocenes*; VCH: Weinheim, Germany, and New York, 1995. For bent-metallocene systems see for example: (b) Bertuleit, A.; Fritze, C.; Erker, G.; Fröhlich, R. *Organometallics* **1997**, *16*, 2891. (c) Bosch, B.; Erker, G.; Fröhlich, R.; Meyer, O. *Organometallics* **1997**, *16*, 5449. (d) Karsch, H. H.; Graf, V.; Reisky, M.; Witt, E. *Eur. J. Inorg. Chem.* **1998**, 1403. (e) Schumann, H.; Rosenthal, E. C. E.; Demtschuk, J.; Molander, G. A. *Organometallics* **1998**, *17*, 5324.

(3) (a) Ganter, C.; Brassat, L.; Glinsböckel, C.; Ganter, B. *Organometallics* **1997**, *16*, 2862. (b) Ganter, C.; Brassat, L.; Ganter, B. *Chem. Ber.* **1997**, *130*, 1771. (c) Ganter, C.; Glinsböckel, C.; Ganter, B. *Eur. J. Inorg. Chem.* **1998**, 1163. (d) Brassat, L.; Ganter, B.; Ganter, C. *Chem. Eur. J.* **1998**, *4*, 2148.

(4) (a) Bildstein, B.; Hradsky, A.; Kopacka, H.; Malleier, R.; Ongania, K.-H. *J. Organomet. Chem.* **1997**, *540*, 127. (b) For the analogous condensation with fluorene see: Wright, M. E.; Cochran, B. B. *Organometallics* **1993**, *12*, 3873.

(5) Isolated as a deep violet powder after evaporation of the methanol and filtration of the residue over a short plug of alumina with hexane. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.27 (s, 3H, CH_3), 2.32 (s, 3 H, CH_3), 4.18 (s, 5 H, Cp), 4.19 (d, $^2J_{PH}$ = 36.6 Hz, 1 H, α-C*H*), 6.20 (d/tr, 1 H, C*H*), 6.45 (d/tr, 1 H, C*H*), 6.60 (m, 1 H, C*H*), 7.00 (br d, 1 H, C*H*), 7.07 (d, $^3J_{PH}$ = 13.1 Hz, 1 H, C*H*). ^{13}C NMR ($CDCl_3$): δ 14.2 (s, 1 C, *C*H$_3$), 17.1 (s, 1 C, *C*H$_3$), 73.4 (s, 5 C, Cp), 80.7 (d, $^1J_{CP}$ = 59.2 Hz, 1 C, α-*C*H), 88.5 (d, $^1J_{CP}$ = 62.6 Hz, 1 C, α-*C*CH), 95.2 (d, $^2J_{CP}$ = 5.0 Hz, 1 C, *C*CH$_3$), 98.0 (d, $^2J_{CP}$ = 7.2 Hz, 1 C, *C*CH$_3$), 121.1 (d, $^4J_{CP}$ = 19.2 Hz, 1 C, H*C*=C (cis)), 126.3 (s, 1 C, H*C* = C (trans)), 128.9 (s, 1 C, H*C*=C), 132.9 (s, 1 C, H*C*=C), 142.0 (d, $^2J_{CP}$ = 15.4 Hz, 1 C, H*C*=C), 143.4 (s, 1 C, HC*C*(CH)$_2$). ^{31}P NMR (CD_2Cl_2): δ −67.9. MS (70 eV): *m*/*z* (%) 308.0 (100%, [M$^+$]), 293.0 (13%, [M$^+$ − CH$_3$]). HRMS: calcd *m*/*z* for $C_{17}H_{17}P^{56}Fe$, 308.04173; found, 308.04166.

(6) To a solution of **2** (685 mg, 2.22 mmol) in hexane (25 mL) was added a solution of 1.58 M $NaBHEt_3$ in THF (2.11 mL, 3.33 mmol, 1.5 equiv) at room temperature. The mixture was stirred for 1 h, and the precipitate was isolated by filtration and washed with hexane to give a yellow-orange powder of Na-**3** (627 mg, 1.89 mmol, 85%) after drying, which was immediately used for the preparation detailed in ref 7.

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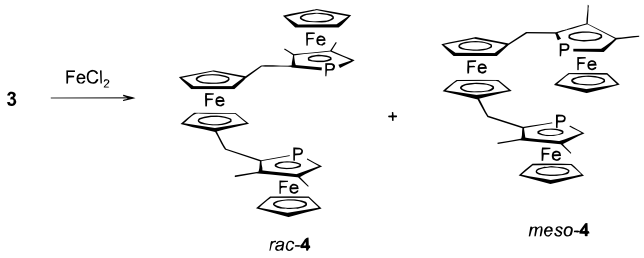
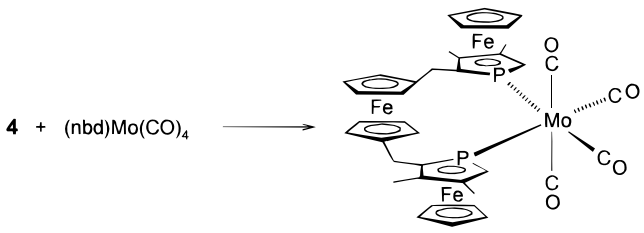
symmetric enantiomers. Analysis of the reaction product



by ^{31}P NMR spectroscopy reveals the *meso* and *rac* isomers to be present in a 1:1 ratio. Of course, when the reaction sequence was carried out with the readily available enantiomerically pure aldehyde (*R*)- or (*S*)-**1** as starting material,[8] the ferrocene **4** was obtained as a single, homochiral enantiomer.

The potential of the bis(phosphaferrocene) **4** to act as a P,P-chelate ligand was proven in the reaction with (nbd)Mo(CO)$_4$ in THF under reflux, leading to the anticipated molybdenum chelate complex **5** in 93% yield.[9] Crystallization of the crude product from hexane



yielded crystals of the complex containig the *rac* ligand suitable for X-ray diffraction.[10] A PLATON plot of the molecular structure of **5** is given in Figure 1 together with selected bond lengths and angles. As expected, the two phosphorus atoms occupy *cis* coordination sites in

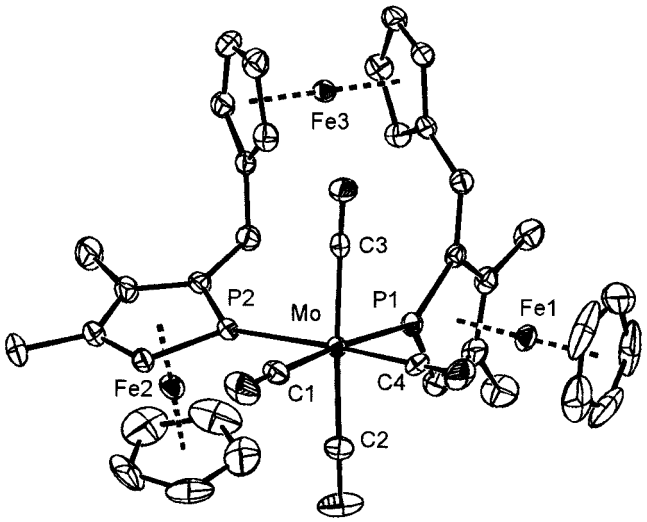


Figure 1. PLATON view of complex **5**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo−P1, 2.518(1); Mo−P2, 2.490(1); Mo−C1, 1.979-(6); Mo−C2, 2.027(6); Mo−C3, 2.044(6); Mo−C4, 1.981(6); P1−Mo−P2, 91.19(5).

the octahedral environment of the molybdenum center. The deviations from regular octahedral geometry are rather small, and the Mo−P and Mo−C distances fall in the range observed for related *cis*-P$_2$Mo(CO)$_4$ complexes.[11] The orientations of the two phosphaferrocene donor groups are such that the CpFe fragments are in an almost parallel alignment with one equatorial and one axial CO ligand, respectively. The central ferrocene unit is located above the equatorial plane made up from the P−Mo−P unit and two additional carbonyl ligands, leading to an overall C_1-symmetric arrangement of the complex. However, in solution we observe effective C_2 symmetry down to −80 °C, as is evident from only one ^{31}P NMR signal and two ^{13}C NMR resonances for the four carbonyl carbons over the entire temperature range.

The free ligand **4** as well as the Mo(CO)$_4$ complex **5** were investigated with regard to their redox properties by cyclic voltammetry.[12] The obtained CV curves are depicted in Figure 2. For the free ligand, two reversible oxidations are observed. The process at lower potential is attributed to the oxidation of the central ferrocene moiety, whereas the second wave is due to the simultaneous oxidation of the two phosphaferrocene moieties. This behavior is in accord with literature reports that phosphaferrocene is oxidized at a slightly higher poten-

(7) To a solution of Na-**3** (0.627 g, 1.89 mmol) in THF was added 0.120 g (0.95 mmol) of solid $FeCl_2$, and the mixture was refluxed overnight. All volatiles were removed, the residue was treated with ether (30 mL), and the solution was filtered over 5 cm of alumina. Evaporation of the solvent gave 0.557 g (0.83 mmol, 87%) of **4** as an orange powder. *rac* and *meso* isomers were formed in a 1:1 ratio and could be distinguished by their ^{31}P NMR spectra only. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.14 (s, 6 H, CH_3), 2.17 (s, 6 H, CH_3), 3.18 (m, 4 H, CH_2), 3.66 (d, $^2J_{PH}$ = 35.7 Hz, 2 H, α-C*H*), 3.91−4.05 (m, 8 H, C*H*), 4.11 (s, 10 H, Cp). ^{13}C NMR ($CDCl_3$): δ 13.9 (s, 2 C, *C*H$_3$), 17.1 (s, 2 C, *C*H$_3$), 30.7 (d, $^2J_{PC}$ = 20.9 Hz, 2 C, *C*H$_2$), 67.9 (s, 2 C, *C*H), 68.0 (s, 2 C, *C*H), 69.0 (s, 2 C, *C*H), 69.1 (s, 2 C, *C*H), 72.0 (s, 10 C, Cp), 75.6 (d, $^1J_{PC}$ = 58.2 Hz, 2 C, α-*C*H), 88.9 (s, 2 C, substituted Cp C_{ipso}), 92.8 (d, $^2J_{PC}$ = 4.4 Hz, 2 C, *C*CH$_3$), 95.6 (d, $^2J_{PC}$ = 6.5 Hz, 2 C, *C*CH$_3$), 99.8 (d, $^1J_{PC}$ = 57.6 Hz, 2 C, α-*C*CH$_2$). ^{31}P NMR ($CDCl_3$): δ −78.75/-78.81 (*rac*/*meso*). MS (70 eV): *m*/*z* (%) 673.9 (5%, [M$^+$]). Anal. Calcd for $C_{34}H_{36}P_2Fe_3$: C, 60.58; H, 5.38. Found: C, 60.42; H, 5.40.

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(9) ^{1}H NMR (500 MHz, $CDCl_3$): *rac*, δ 2.18 (s, 6H, CH_3), 2.24 (s, 6 H, CH_3), 2.84 (m, 2 H, CH_2), 3.06 (m, 2 H, CH_2), 3.44 (br s, 2 H, C*H*), 3.74 (br s, 2 H, C*H*), 3.84 (br s, 2 H, C*H*), 3.86 (d, $^2J_{PH}$ = 31.7 Hz, 2 H, α-C*H*), 3.96 (br s, 2 H, C*H*), 4.26 (s, 10 H, Cp); *meso*, δ 2.09 (s, 6 H, CH_3), 2.14 (s, 6 H, CH_3), 2.94 (m, 2 H, CH_2), 3.35 (m, 2 H, CH_2), 3.41 (br s, 2 H, C*H*), 3.61 (d, $^2J_{PH}$ = 31.4 Hz, 2 H, α-C*H*), 3.74 (br s, 2 H, C*H*), 3.90 (br s, 2 H, C*H*), 3.98 (br s, 2 H, C*H*), 4.27 (s, 10 H, Cp). ^{13}C NMR (500 MHz, CH_2Cl_2, 24 °C): *rac*, δ 14.9 (s, 2 C, *C*H$_3$), 16.7 (s, 2 C, *C*H$_3$), 27.8 (d, $^2J_{PC}$ = 9.9 Hz, 1 C, *C*H$_2$), 27.9 (d, $^2J_{PC}$ = 9.3 Hz, 1 C, *C*H$_2$), 65.7 (s, 2 C, *C*H), 66.6 (s, 2 C, *C*H), 70.0 (s, 2 C, *C*H), 71.0 (s, 2 C, *C*H), 73.4 (d, $^1J_{PC}$ = 41.7 Hz, 2 C, α-*C*H), 73.7 (s, 10 C, *C*H), 89.5 (s, 2 C, C_{ipso} substituted Cp), 90.9 (s, 2 C, *C*CH$_3$), 93.3 (d, $^1J_{PC}$ = 45.5 Hz, 2 C, α-*C*CH$_2$), 94.0 (s, 2 C, *C*CH$_3$), 207. 6 (d/d, $^2J_{PC}$ = 10.4 Hz, $^2J_{PC}$ = 11.0 Hz, 2 C, *C*O), 212.3 (d/d, $^2J_{PC}$ = 9.8 Hz, $^2J_{PC}$ = 13.2 Hz, 2 C, *C*O). ^{31}P NMR ($CDCl_3$): δ −26.55 (*rac*), −22.48 (*meso*). Anal. Calcd for $C_{38}H_{36}O_4P_2Fe_3Mo$: C, 51.74; H, 4.11. Found: C, 51.85; H, 4.18.

(10) Crystal data for $C_{38}H_{36}Fe_3MoO_4P_2$ (**5**): monoclinic, $P2_1/c$ (No. 14), a = 16.365(6) Å, b = 11.639(2) Å, c = 20.13(2) Å, β = 109.48(5)°, V = 3615(3) Å^3, Z = 4, D_c = 1.62 g cm^{-3}, T = 293 K, Mo Kα, 6330 unique reflections, Enraf-Nonius CAD4, crystal size 0.3 × 0.2 × 0.2 mm^3, R = 0.046, R_w = 0.037 for 4652 observed reflections ($I > \sigma(I)$). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136784. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, int. +1223/336-033; E-mail, teched@chemcrys.cam.ac.uk).

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(12) Conditions: CH_2Cl_2 solution, ca. 10^{-3} mol/L, NBu_4PF_6 as supporting electrolyte, scan rate 100 mV/s, measured versus SCE (with Fc^+/Fc = 0.4 V under experimental conditions).

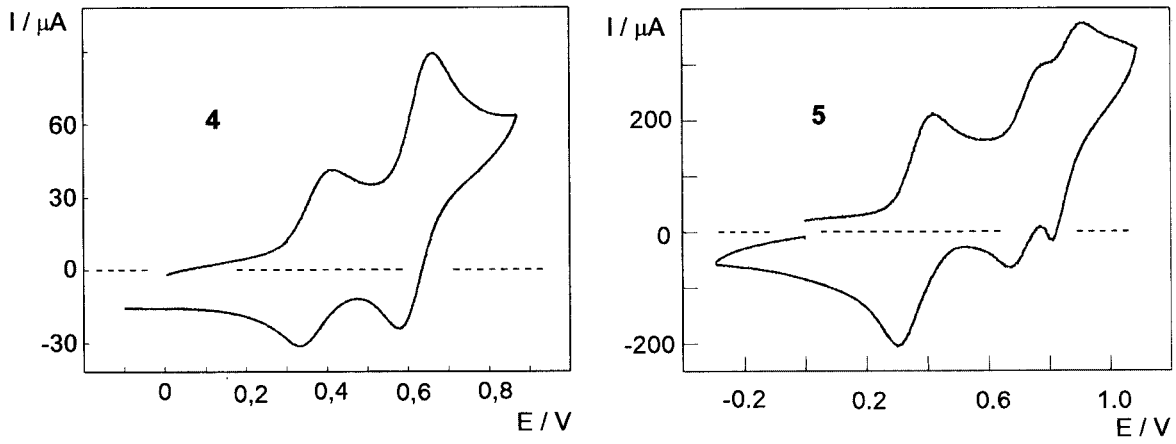
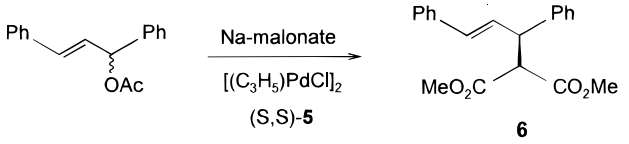


Figure 2. Cyclic voltammograms of compounds **4** and **5** in CH_2Cl_2 at 100 mV/s. Potentials are given versus SCE.

tial than ferrocene.[13] A qualitatively different CV is observed for the molybdenum complex. Again, the wave at lower potential is associated with the oxidation of the ferrocene core of the ligand. However, the two phosphaferrocene moieties are no longer independent but instead are electronically coupled by the connection via the central molybdenum atom, leading to two distinct reversible oxidation processes, which are not fully resolved.

The compound (*S*,*S*)-**5**, which was prepared from the enantiomerically pure aldehyde (*S*)-**1**, was tested as a chiral ligand in the catalytic asymmetric allylic substitution.[14] When 1,3-diphenylallyl acetate was treated with sodium malonate in the presence of $[(C_3H_5)PdCl]_2$ (1%) and ligand **5** (2%), the substitution product **6** was obtained in 78% isolated yield and with 79% ee.[15] Our



previous studies of the use of chiral C_1-symmetric phosphaferrocene-based P,P- or P,N-ligands in the catalytic asymmetric allylic substitution have so far given low ee values of ≤20%, so that the new ligand reported in this communication constitutes a significant progress for us regarding the selectivity in this reaction. We are currently exploring the potential of the anion **3** for the preparation of other sandwich and half-sandwich complexes and their application in catalytic enantioselective reactions.

Acknowledgment. Support of this work by the Deutsche Forschungsgemeinschaft (SFB 380) is gratefully acknowledged. We thank Prof. U. Kölle for his help with the CV measurements.

Supporting Information Available: Complete X-ray crystallographic data for the structure of compound **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM9905207

(13) Lemoine, P.; Gross, M.; Braunstein, P.; Mathey, F.; Deschamps, B.; Nelson, J. H. *Organometallics* **1984**, *3*, 1303.

(14) For a comprehensive recent review see: Trost, B. M.; van Vrancken, D. L. *Chem. Rev.* **1996**, *96*, 395.

(15) *Experimental Procedure:* $[(C_3H_5)PdCl]_2$ (1.8 mg, 0.005 mmol), ligand **4** (6.7 mg, 0.01 mmol), and 1,3-diphenyl-2-propenyl acetate (126 mg, 0.5 mmol) were dissolved in THF (5 mL). To this solution was added a solution of sodium malonate, prepared from dimethyl malonate (132 mg, 1.0 mmol) in THF (5 mL) and NaH (24 mg, 1.0 mmol), via syringe. The mixture was stirred for 15 h, acetic acid (1 mL) was added, and the solvent was removed in vacuo. Water was added, the mixture was extracted with Et_2O, the organic layer was washed with water and brine and dried with Na_2SO_4, and the solvent was removed in vacuo. The resulting yellow oil was purified by chromatography on silica with hexane/ethyl acetate (5:1) to yield pure product **6** (126 mg, 78%). The enantiomeric excess was determined by HPLC to be 79%. (Daicel CHIRALCEL OD with 100:1 hexane/2-propanol as eluent, flow 0.5 mL/min, t_1 = 15.87 min, t_2 = 17.00 min). The NMR data are consistent with the literature data.[16]

(16) Brown, J. M.; Hulmes, D. I.; Guiry, P. J. *Tetrahedron* **1994**, *15*, 4499.