Fulvene-Like Cationic Phosphaferrocene Species as Synthetically Valuable Intermediates: Preparative and Mechanistic Aspects of the Diastereoselective Formation of α-Phosphanyl-Substituted 2-Ethylphosphaferrocenes

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Abstract: Addition of MeMgI to the sandwich aldehyde **1** proceeds diastereoselectively to yield the alcohol **2a**, which undergoes protonation and subsequent elimination of water to give the cationic fulvene-like species (*E*)-**7**. Reaction of (*E*)-**7** with a nucleophile yields the corresponding substitution product with retention of configuration. In the absence of any nucleophile, (*E*)-**7** isomerizes to the thermodynamically more stable species (*Z*)-**7**. The rate constant for this reaction has been determined as $k = 0.037(3)\ min^{-1}$ at $-40\,^{\circ}C$. Treatment of the cation (*Z*)-**7** with a nucleophile produces the diastereomeric substitution product with inversion of configuration at the stereogenic centre in comparison with the starting alcohol **2a**. The phosphine **6b** obtained by reaction of (*Z*)-**7** with $HPCy_2$ acts as a *P,P*-chelate ligand in the complex [**6b** · $Mo(CO)_4$] (**11**), which was characterized by X-ray structural analysis. The crystal structure determination confirmed the configurational assignments made on the basis of NMR spectroscopic data.

Keywords: chelates · phosphaferrocenes · phosphorus heterocycles · P ligands · sandwich complexes

Introduction

Ferrocenyldiphosphines play a major role as chiral *P,P*-chelate ligands.[1] Most of these ferrocenyl systems contain a planar as well as a central element of chirality. Recently, we have shown substituted phosphaferrocenes to be a new class of chelate ligands with planar chirality that are able to coordinate through both the phospholyl P atom and a further donor substituent attached to the phospholyl ring.[2, 3] We have prepared and characterized several such complexes with *P,N*- and *P,P*-ligands. By analogy with the ferrocene derivatives, we were interested in introducing an additional stereogenic centre into this novel type of ligand. This paper describes a synthetic strategy for the preparation of α-phosphanyl-substituted 2-ethylphosphaferrocenes with high diastereoselectivity. Choice of appropriate reaction conditions allows control of the relative configuration of the newly created stereogenic centre. The *E–Z* isomerization of a cationic fulvene-like intermediate was monitored using ^{31}P NMR spectroscopy, from which the barrier to internal rotation about the partial C=C double bond was determined.

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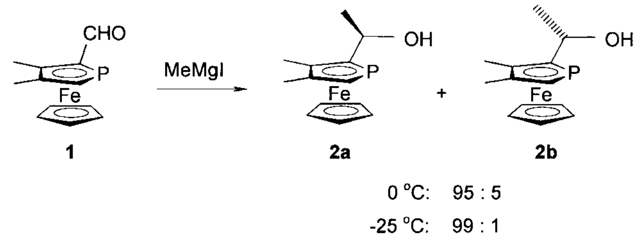
Results

Diastereoselective addition to the aldehyde 1: 2-Formyl-3,4-dimethylphosphaferrocene (**1**) has proved to be a versatile starting material for the preparation of a number of differently substituted phosphaferrocene chelate ligands with *N*- and *P*-donor atoms.[2, 3] Furthermore, **1** is readily available in enantiomerically pure form in multigram quantities[4] and this, in turn, allows synthesis of the respective ligands as pure enantiomers. Introduction of the new stereogenic centre could be achieved by nucleophilic attack on either of the diastereotopic faces of the carbonyl group of **1**. Treatment of **1** with MeMgI (1.5 equiv) in ether at 0 °C afforded the diastereomeric alcohols **2a** and **2b** (95:5, Scheme 1), which were separated by chromatography on alumina. The diastereomers are easily distinguished by their ^{31}P and ^{1}H NMR spectra [$\delta(^{31}P) = -91.0$ (**2a**), -84.6 (**2b**)]. In the ^{1}H NMR spectra the



Scheme 1.

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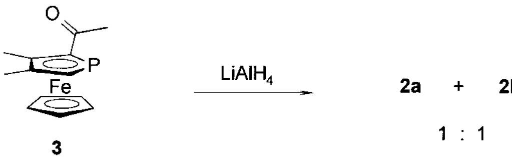
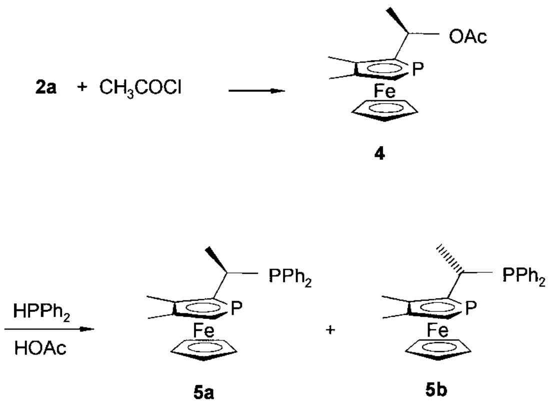
resonances for the methyl group of the side chain appear at $\delta = 1.27$ and 1.45, respectively. If the reaction is carried out at $-25\,^{\circ}C$, the ratio of the diastereomers becomes 99:1 (**2a**:**2b**). The relative configuration of the alcohols is discussed later. Interestingly, the reaction of $LiAlH_4$ with 2-acetylphosphaferrocene (**3**) (as reported by Roberts et al.[5]) proceeds without selectivity to give **2a** and **2b** in a 1:1 ratio (Scheme 2).



Scheme 2.

Nucleophilic substitution of the hydroxyl group of alcohol 2: Having established the route to the diastereomerically pure alcohol **2a**, we next turned our attention to the transformation of the hydroxyl group into a more valuable phosphanyl moiety. Hayashi et al. have developed a method for facile conversion of ferrocenyl alcohols into phosphines by treating the corresponding acetates with a secondary phosphine, HPR_2.[6] Reaction of the phosphaferrocene alcohol **2a** with acetyl chloride yielded the acetate **4**, which could not be purified by chromatography as it undergoes elimination reactions (Scheme 3). Nevertheless, the ^{31}P NMR spectrum of the crude product showed the presence of a single diastereomer. Treatment of **4** with diphenylphosphine in glacial acetic acid under reflux gave the corresponding derivative **5** in 70% yield. Its ^{1}H and ^{31}P NMR spectra revealed the presence of two diastereomers **5a** and **5b** in a 55:45 ratio. Considerable epimerization of the stereogenic centre was, therefore, observed in the substitution reaction of **4** under these conditions.

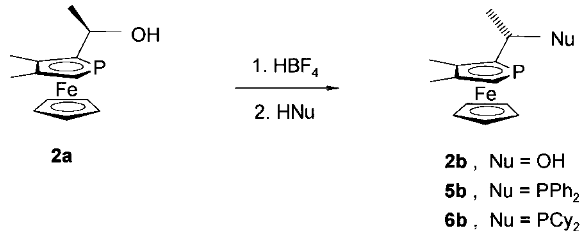
A different approach to the diastereomerically pure phosphanyl compound **5** involved protonation of the OH group and subsequent elimination of water. This yielded a cationic intermediate that was treated with a secondary



Scheme 3.

phosphine as the nucleophile. For the analogous ferrocene compounds, such transformations occur cleanly and with retention of configuration at the pseudobenzylic C atom.[7] Roberts et al. have reported the protonation of a diastereomeric mixture of the phosphaferrocenyl alcohols **2a** and **2b** in solution in CF_3COOH. Their cationic reaction product could not be fully investigated owing to problems of decomposition, and only ^{31}P NMR data were obtained.[5] However, we found that the cationic species is stable in CH_2Cl_2 for hours at ambient temperature. Consequently, it provides an excellent intermediate for the preparation of substitution products.

Addition of HBF_4 (1.2 equiv) to pure phosphaferrocenyl alcohol **2a** in CH_2Cl_2 at $0\,^{\circ}C$ gave a dark red solution. Once the solution had been stirred for 15 min, $HPPh_2$ (2.0 equiv) was introduced into the mixture, which immediately became orange. Following aqueous work-up and chromatographic purification, the phosphanyl-substituted phosphaferrocene **5b** was obtained in almost quantitative yield as a single diastereomer. Its ^{31}P NMR spectrum features two doublets at $\delta = -82.9$ and 11.6 [$J(P,P) = 26.0$ Hz]. Use of $HPCy_2$ in place of $HPPh_2$ produced the analogous dicyclohexylphosphanyl compound **6b** (Scheme 4). Similarly, with H_2O as the nucleophile,



Scheme 4.

the diastereomeric alcohol **2b** is formed quantitatively after work-up, with no traces of the starting material **2a** detectable in the ^{1}H and ^{31}P NMR spectra. Furthermore, the same diastereomerically pure compound **2b** is obtained if the reaction sequence is performed using an initial mixture of diastereomers **2a** and **2b** (prepared by reduction of the acetyl compound **3** by $LiAlH_4$). Scheme 5 depicts our proposed mechanistic explanation of these findings. By comparison with the analogous ferrocene compounds,[7b] we propose that loss of a water molecule from the protonated alcohol occurs

Abstract in German: *Die Addition von MeMgI an den Aldehyd **1** verläuft diastereoselektiv unter Bildung des Alkohols **2**, der durch Protonierung und Wasserabspaltung in die kationische, Fulven-analoge Spezies (E)-**7** umgewandelt werden kann. Die Reaktion des Kations (E)-**7** mit Nucleophilen ergibt die entsprechenden Substitutionsprodukte unter Retention. In Abwesenheit nucleophiler Agentien lagert sich das Kation (E)-**7** in die thermodynamisch stabilere Verbindung (Z)-**7** um. Die Geschwindigkeitskonstante für diesen Isomerisierungsprozeß beträgt k = 0.037(3) min^{-1} bei $-40\,^{\circ}C$. Durch Reaktion des Kations (Z)-**7** mit Nucleophilen werden nun Substitutionsprodukte unter Inversion der Konfiguration erhalten. Das Phosphin **6b**, das aus (Z)-**7** und $HPCy_2$ gewonnen wurde, fungiert als P,P-Chelatligand im Komplex [**6b**·Mo(CO)$_4$] (**11**), der durch Kristallstrukturanalyse charakterisiert wurde. Die Strukturbestimmung bestätigt die Konfigurationszuordnungen, die auf der Basis NMR-spektroskopischer Daten getroffen wurden.*

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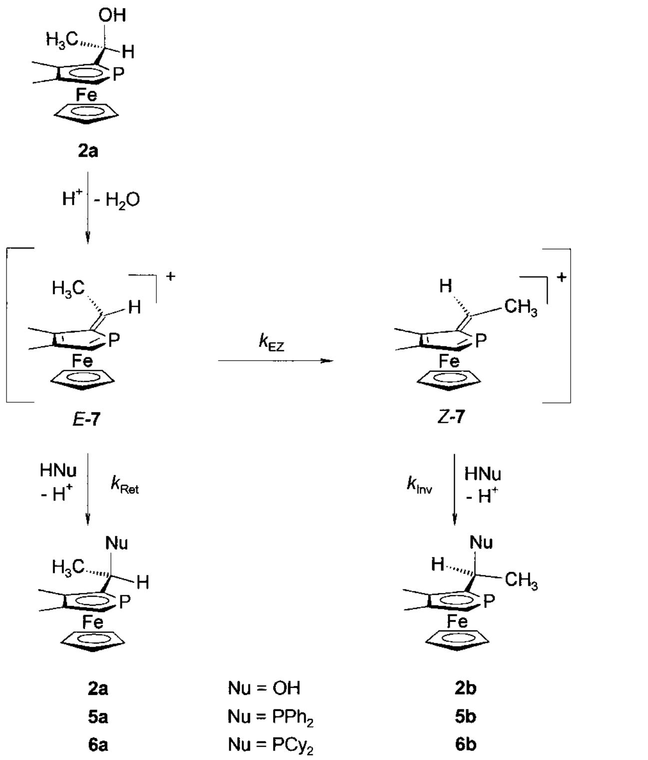
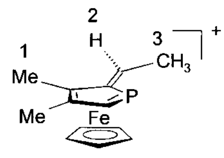


Scheme 5. Proposed mechanism for the formation of diastereomeric substitution products.

selectively *trans* to the CpFe fragment. The diastereomerically pure alcohol **2a** is thus converted to a fulvene-like cation with an *E* arrangement of the phosphorus atom and the methyl group with respect to the exocyclic C−C bond. The fate of this intermediate depends on the reaction conditions. In the absence of a nucleophilic reagent (that is, when the solution is simply stirred for 15 min prior to the addition of the nucleophile as described above) the species (*E*)-**7** isomerizes to (*Z*)-**7**. The driving force for this isomerization is the relief of the sterically unfavourable interaction between two methyl groups: one located in the 3-position of the phospholyl ring, the other on the pseudobenzylic C atom. Addition of a nucleophile to the fulvene-like C atom exclusively from the direction opposite to the CpFe moiety leads to a substitution product with an inverted configuration at the pseudobenzylic centre compared with the starting material. In contrast, if a nucleophile is present when (*E*)-**7** is formed, the stereochemical outcome of the substitution reaction depends on whether or not the isomerization of the cation to (*Z*)-**7** is faster than the reaction with the nucleophile (c.f. the Curtin–Hammett principles[8]). For reactions where the nucleophile reacts with (*E*)-**7** before isomerization can occur, the substitution product should be formed with retention of configuration at the benzylic centre.

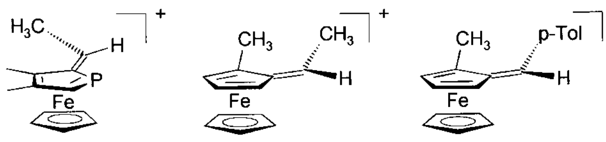
Several experimental facts lend further weight to our mechanistic proposal.

1) If the cation (*E*)-**7** is formed from the alcohol **2a** in the presence of a nucleophile, the retention product is indeed formed in excess. For example, with $HPPh_2$ at 0 °C the diastereomeric phosphines **5a** and **5b** are obtained in a ratio of 80:20. The proportion of retention product is enhanced by lowering the reaction temperature (−78 °C, 90:10; −90 °C, 95:5). With $HPCy_2$ under the same conditions the dicyclohexylphosphines **6a** and **6b** are formed with somewhat lower diastereoselectivity (−90 °C, 90:10). The slower reaction rate with $HPCy_2$ may be a result of the larger cone angle of this phosphine.
2) The isomerization of (*E*)-**7** to (*Z*)-**7** can be monitored by ^{31}P NMR spectroscopy at −40 °C in CD_2Cl_2. A plot of $\ln x$ (x = mole fraction of (*Z*)-**7**) against time indicates a first-order reaction with a rate constant of $k_{EZ} = 0.037(3)$ min^{-1}. After equilibration, the starting species (*E*)-**7** is no longer detectable. With the NMR detection limit taken as ca. 1 %, the equilibrium constant $K_{[(Z)\text{-}\mathbf{7}/(E)\text{-}\mathbf{7}]}$ is estimated to be at least ≈100.
3) The relative configuration of the thermodynamically more stable species (*Z*)-**7** can be determined by NOE measurements. Irradiation of the resonance attributable to the phospholyl methyl group 1 produces a NOE for the signal of proton 2, but not for the methyl group 3 in the fulvene position.



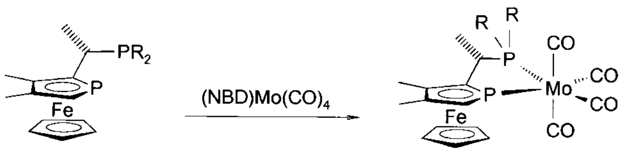
4) Further evidence for the configurational assignments is provided by the X-ray diffraction study of [**6b** · Mo(CO)$_4$] (**11**), a derivative of (*Z*)-**7** (see Complexation Studies below).

In the ^{1}H NMR spectrum of (*Z*)-**7** several signals are shifted downfield with respect to those of the starting alcohol **2a**. In particular, the phospholyl α proton signal is shifted from δ = 3.76 to 6.16, and the signal for the fulvene H appears at δ = 6.98. An additional downfield shift of ca. 60 ppm is noted in the ^{31}P NMR spectrum of (*Z*)-**7**. According to the Eyring equation, the rate constant for the fulvene isomerization of [$k_{EZ} = 0.037(3)$ min^{-1}] corresponds to a free energy of activation of $\Delta G^{\neq} = 74(4)$ kJ mol^{-1} for internal rotation about the partial C=C double bond. For the comparable ferrocene derivative **8**, Watts[9] reported a value of $\Delta G^{\neq} = 104(3)$ kJ mol^{-1}. Obviously, description of the cation as a fulvene with enhanced double-bond character is more applicable to the ferrocene species. However, the situation may depend strongly on the nature of the substituents on the fulvene carbon, as demonstrated by the fast *E*–*Z* isomerization of the *p*-tolyl-substituted ferrocenyl cation **9** reported by Kagan.[10]



(*E*)-**7** **8** **9**

Complexation studies: The phosphanyl-substituted phosphaferrocenes **5b** and **6b** were reacted with different metal fragments in order to examine their potential as *P,P*-chelating ligands. When ligand **5b** was refluxed with [(NBD)Mo(CO)$_4$] in THF for 2 h, the chelate complex [**5b** · Mo(CO)$_4$] (**10**) was isolated in quantitative yield as an orange powder (Scheme 6). The ^{31}P NMR spectrum of complex **10** shows two doublets shifted downfield to δ = −0.5 and 79.7, with a coupling



5b, R = Ph
6b, R = Cy

10, R = Ph
11, R = Cy

Scheme 6.

constant of J(P,P) = 7.1 Hz. The analogous complex **11** (containing the dicyclohexylphosphanyl-substituted ligand **6b**) showed similar spectroscopic trends. Orange needles of complex **11,** suitable for X-ray diffraction, were obtained by recrystallization from diethyl ether/hexane. A PLATON plot of the structure of **11** is depicted in Figure 1, together with

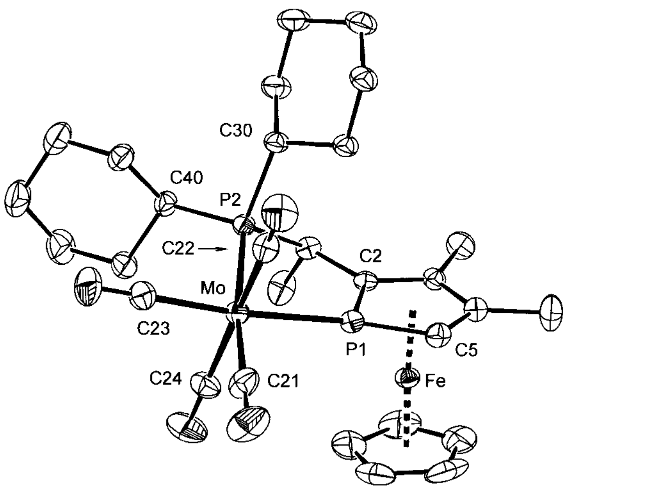


Figure 1. Molecular structure (PLATON) of complex **11**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°], with estimated standard deviations in parentheses: Mo–P1 2.4654(9), Mo–P2 2.5735(9), Mo–C21 1.973(4), Mo–C22 2.025(4), Mo–C23 1.988(4), Mo–C24 2.050(4); P1-Mo-P2 74.78(3), Mo-P1-C2 115.4(1), Mo-P1-C5 152.0(1), C2-P1-C5 90.8(2).

selected bond lengths and angles. The structure determination reveals unambiguously the relative configuration of both the planar and the central elements of chirality, and thus confirms the assignment made on the basis of the spectroscopic data outlined earlier. Apart from the orientation of the two cyclohexyl groups, the geometric parameters of the structure are similar to those found for the $Mo(CO)_4$ complex with $PFcCH_2PCy_2$.[3] The Mo–P bond length is shorter for the better acceptor P1 (2.465(1) Å) than for the better donor P2 (2.574(1) Å). The bite angle P1-Mo-P2 of 74.78(3)° reveals a severe deviation from octahedral coordination about the Mo centre.

Conclusion

Cationic fulvene-like phosphaferrocene species are easily accessible from the diastereomerically pure alcohol **2a** by protonation and elimination of water, and therefore constitute a new class of stable intermediates of great synthetic potential. The slow but quantitative isomerization of the initial cation (E)-**7** to the thermodynamically more stable (Z)-**7** permits synthesis of products with retention or inversion of configuration, as either isomer can undergo nucleophilic attack. Configurational assignments were made on the basis of NMR data, and were confirmed by the X-ray structure determination of complex **11**. The barrier to internal rotation about the fulvene C–C bond in (E)-**7** was found to be considerably lower than for the analogous ferrocene compound. We are currently trying to obtain (Z)- and (E)-**7** in crystalline form and to explore their potential for further applications.

Experimental Section

All experiments were carried out under dry nitrogen with standard Schlenk equipment. Compounds **1**[11] and **3**[12] were prepared as reported in the literature. NMR spectra were recorded on a Varian Unity 500 (^{1}H, 500 MHz; ^{13}C{^{1}H} 125 MHz; ^{31}P{^{1}H} 202 MHz) or a Bruker WP 80-SY spectrometer (^{1}H, 80 MHz; ^{31}P{^{1}H} 32 MHz). MS: Finnigan MAT 95 (EI, 70 eV). IR: Perkin–Elmer 1720X. Elemental analyses were performed with a Carlo–Erba elemental analyzer 1106.

(R_P,R)/(S_P,S)-1-(3,4-Dimethylphosphaferrocen-2-yl)ethanol (**2a**): Aldehyde **1** (850 mg, 3.27 mmol) in ether (5 mL) was added to a freshly prepared solution of MeMgI (4.6 mmol) in ether (20 mL) at −30 °C. This solution was allowed to warm to room temperature and was then gently refluxed on a water bath for 1 h. Water (20 mL) was added, and the solution was acidified with dilute HCl. The organic layer was separated and washed with water and brine, while the aqueous layer was extracted with ether. The collected organic layers were dried with Na_2SO_4. The solvent was then removed to yield a dark orange residue which was purified by column chromatography (hexane/ether = 2:1) to afford **2a** (885 mg, 3.20 mmol, 98%) as a dark orange oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (d, J = 6.1 Hz, 3H; CHCH_3), 1.75 (brs, 1H; OH), 2.13 (s, 3H; CH_3), 2.20 (s, 3H; CH_3), 3.76 (d, J = 36.6 Hz, 1H; PCH), 4.14 (s, 5H; Cp), 4.44 (dq, J = 6.1 Hz, J = 1.4 Hz, 1H; CH); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 12.8 (s, CH_3), 15.8 (s, CH_3), 24.9 (d, J(PC) = 3.6 Hz; CHCH_3), 66.7 (d, J = 13.5 Hz; CH), 70.8 (s, Cp), 74.7 (d, J = 57.9 Hz; CH), 90.7 (d, J = 5.5 Hz; CH_3), 95.8 (d, J = 6.7 Hz; CH_3), 107.2 (d, J = 59.2 Hz; P=C); ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ = −91.0 (s); MS: m/z = 276 (M^+, 100%), 258 ($[M-H_2O]^+$, 80%); $C_{13}H_{17}PO^{56}Fe$ (276.1): calcd C 56.55, H 6.21; found C 55.90, H 6.53; HRMS calcd 276.03679; found 276.03711.

(R_P,S)/(S_P,R)-1-(3,4-Dimethylphosphaferrocen-2-yl)ethanol (**2b**): HBF_4 (55% in ether, 0.1 mL, 0.56 mmol) was added to a solution of **2a** (110 mg, 0.40 mmol) and $(CH_3CO)_2O$ (0.05 mL, 0.56 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The colour of the solution changed from orange to dark red. After 10 min, water (10 mL) was added and the colour of the solution changed back to orange. The layers were separated and the organic phase was washed with water and dried over Na_2SO_4. Evaporation of the solvent gave an orange oil, which was eluted with hexane/ether (2:1) to afford **2b** (70 mg, 0.25 mmol, 63%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.45 (d, J = 6.1 Hz, 3H; CHCH_3); 2.16 (s, 3H; CH_3); 2.18 (s, 3H; CH_3); 3.43 (m, 1H; CH); 3.72 (d, J = 36.6 Hz, 1H; P=CH); 4.08 (s, 5H; Cp); 4.20 (brs, 1H; OH); ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) δ = −84.6 (s); MS: m/z = 276 (M^+, 100%), 258 ($[M-H_2O]^+$, 80%); $C_{13}H_{17}PO^{56}Fe$: calcd 276.03679, found 276.03722 (HRMS).

(R_P,R)/(S_P,S)-[1-(3,4-Dimethylphosphaferrocen-2-yl)ethyl]diphenylphosphine (**5a**): HBF_4 (55% in ether, 0.1 mL, 0.69 mmol) was added dropwise to a solution in CH_2Cl_2 containing **2a** (134 mg, 0.49 mmol), $(CH_3CO)_2O$ (0.07 mL, 0.69 mmol) and $HPPh_2$ (2.0 equiv) at −90 °C. The mixture was stirred at 0 °C for 30 min and subsequently for 2 h at room temperature. Dilute NaOH (10 mL) was added and the organic layer was separated, washed with water and brine, and then dried over Na_2SO_4. After removal of the solvent, the resulting brown oil was purified by chromatography on Al_2O_3 (hexane/diethyl ether = 8:1) to yield **5** (223 mg, 0.49 mmol, 99%) as a mixture of both diastereomers (**5a**:**5b** = 95:5). These isomers were separated chromatographically on Al_2O_3 (hexane/diethyl ether = 15:1) to give **5a** (191 mg, 0.42 mmol, 85%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (m, 3H; CH_3); 2.06 (s, 3H; CH_3); 2.15 (s, 3H; CH_3); 3.40 (m, 1H; CHPPh$_2$);

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3.68 (d, $J=36.6$ Hz, 1H; P=CH); 4.16 (s, 5H; Cp); 6.80-7.50 (m, 10H; phenyl-H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta=14.2$ (dd, $J=9.6$, 30.6 Hz; $CHCH_3$); 17.0 (s, CH_3); 21.9 (s, CH_3); 33.1 (s, CH_3); 72.0 (s, Cp); 75.9 (d, $J=58.0$ Hz; α-CH); 92.0 (s, β-C); 95.8 (s, β-C); 104.8 (dd, $J=56.7$ Hz, $J=21.4$ Hz; α-C); 128.0-134.0 (m, 8C; C-phenyl); 136.8 (d, $J=15.5$ Hz; C_{ipso}); 137.8 (d, $J=12.9$ Hz; C_{ipso}); $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): $\delta=-76.5$ (d, $J=66.8$ Hz; cycl. P); -0.9 (d, $J=66.8$ Hz; PPh_2); MS: $m/z=444$ (M^+, 20%); 259 ($[M-PPh_2]^+$, 100%); 185 ($[PPh_2]^+$, 20%); $C_{25}H_{26}P_2{}^{56}Fe$: calcd 444.0859, found 444.0840 (HRMS).

(R_P,S)/(S_P,R)-[1-(3,4-Dimethylphosphaferrocen-2-yl)ethyl]diphenylphosphine (5b): HBF_4 (1.2 equiv, 55% in ether) was added to a solution of **2a** (150 mg, 0.55 mmol) and $(CH_3CO)_2O$ (1.2 equiv) in CH_2Cl_2 (10 mL) at 0°C. After stirring at 0°C for 15 min, $HPPh_2$ (2.0 equiv) was added. Further stirring for 30 min was followed by quenching with diluted NaOH (10 mL). The organic layer was separated, washed with water and brine, and then dried over Na_2SO_4. Removal of the solvent in vacuo produced a brown oil, which was purified by chromatography on Al_2O_3 (hexane:ether = 8:1) to yield **5b** (250 mg, 0.55 mmol, 99%). ^1H NMR (500 MHz, $CDCl_3$): $\delta=1.26$ (s, 3H; CH_3); 1.32 (m, 3H; CH_3); 1.96 (s, 3H; CH_3); 3.00 (m, 1H; $CHPPh_2$); 3.67 (d, $J=36.6$ Hz, 1H; P=CH); 3.98 (s, 5H; Cp); 6.80–7.50 (m, 10H; phenyl-H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta=12.8$ (s, CH_3); 14.3 (s, CH_3); 15.9 (dd, $J(C,P)=12.4$, 17.7 Hz; $CHCH_3$); 32.1 (dd, $J(C,P)=13.3$, 14.0 Hz; $CHPPh_2$); 72.0 (s, Cp); 75.7 (d, $J(C,P)=57.8$ Hz; α-CH); 92.0 (d, $J(C,P)=5.7$ Hz; β-C); 94.4 (d, $J(C,P)=6.7$ Hz; β-C); 105.0 (dd, $J(C,P)=57$, 16 Hz; α-C); 126.2 (s, CH); 127.0 (s, CH); 127.3 (s, CH); 127.4 (s, CH); 127.6 (s, CH); 128.2 (s, CH); 131.8 (d, $J(C,P)=16.0$ Hz; CH); 132.2 (d, $J(C,P)=19.3$ Hz; CH); 134.8 (d, $J(C,P)=25.8$ Hz; C_{ipso}); 136.4 (d, $J(C,P)=24.0$ Hz, C_{ipso}); $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): $\delta=-82.9$ (d, $J(P,P)=26.0$ Hz; cycl. P); 11.6 (d, $J(P,P)=26.0$ Hz; PPh_2); MS: $m/z=444$ (M^+, 20%); 259 ($[M-PPh_2]^+$, 100%); 185 ($[PPh_2]^+$, 20%); $C_{25}H_{26}P_2Fe$ (444.3): calcd C 67.59, H 5.90; found C 67.31, H 5.91.

(R_P,R)/(S_P,S)-[1-(3,4-Dimethylphosphaferrocen-2-yl)ethyl]dicyclohexylphosphine (6a): A solution of **2a** (134 mg, 0.49 mmol) and $HPCy_2$ (2.0 equiv) in CH_2Cl_2 was treated at -90°C as described in the preparation of **5a** (see above), to yield a mixture of the diastereomers **6a** and **6b** (90:10). It was not possible to separate them by chromatography. (±)-**6a**: ^1H NMR (500 MHz C_6D_6): $\delta=0.90$–2.40 (m, 22H; cyclohexyl-H); 1.23 (m, 3H; CH_3); 1.95 (s, 3H; CH_3); 2.07 (s, 3H; CH_3); 2.63 (m, 1H; CH); 3.62 (d, $J=35.9$ Hz, 1H; P=CH); 4.12 (s, 5H; Cp); $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): $\delta=14.7$ (s, CH_3); 17.0 (s, CH_3); 20.9 (s, CH_3); 27.0 (s, CH_2); 27.4 (s, CH_2); 27.7 (d, $J=10.4$ Hz; CH_2); 27.9 (d, $J=8.0$ Hz; CH_2); 28.0 (d, $J=6.8$ Hz; CH_2); 28.3 (d, $J=14.3$ Hz; CH_2); 29.0 (s, CH_2); 29.4 (d, $J=21.0$; $CHPCy_2$); 30.3 (d, $J=10.1$ Hz; CH_2); 30.8 (d, $J=7.1$ Hz; CH_2); 31.9 (d, $J=15.7$ Hz; CH_2); 32.3 (d, $J=18.0$ Hz; C_{ipso}-cyclohexyl); 34.1 (d, $J=6.0$ Hz; CH_2); 34.6 (d, $J=20.9$ Hz; C_{ipso}-cyclohexyl); 72.5 (s, Cp); 76.1 (d, $J=59.3$ Hz; α-CH); 92.6 (s, β-C); 95.4 (d, $J=5.9$ Hz; β-C); 107.4 (dd, $J=17.3$, 60.4 Hz; α-C); $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): $\delta=-74.9$ (d, $J=44.5$ Hz; cycl. P); 10.4 (d, $J=44.5$ Hz; PCy_2); MS: $m/z=456$ (M^+, 20%); 259 ($[M-PCy_2]^+$, 100%); $C_{25}H_{38}P_2{}^{56}Fe$: calcd 456.179815; found 456.180010 (HRMS).

(R_P,S)/(S_P,R)-[1-(3,4-Dimethylphosphaferrocen-2-yl)ethyl]dicyclohexylphosphine (6b): Compound **2a** (150 mg, 0.55 mmol) and $HPCy_2$ (2.0 equiv) were treated as described above for **5b** to give **6b** (246 mg, 0.54 mmol, 98%). The compound is decomposed by $CDCl_3$. ^1H NMR (500 MHz, C_6D_6): $\delta=0.95$–1.95 (m, 22H; cyclohexyl-H); 1.55 (dd, $J=7.4$, 7.0 Hz, 3H; $CHCH_3$); 1.90 (s, 3H; CH_3); 2.25 (s, 3H; CH_3); 2.74 (m, 1H; $CHPCy_2$); 3.63 (d, $J=36.7$ Hz, 1H; P=CH); 3.93 (s, 5H; Cp); $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): $\delta=15.3$ (d, $J=5.3$ Hz; CH_3); 16.9 (s, CH_3); 18.6 (d, $J=16.2$; $CHPCy_2$); 25.8 (s, CH_2); 26.9 (d, $J=4.9$ Hz; CH_2); 27.2 (d, $J=10.9$ Hz; CH_2); 27.5 (d, $J=7.4$ Hz; CH_2); 28.2 (d, $J=5.3$ Hz; CH_2); 30.3 (d, $J=10.6$ Hz; CH_2); 30.5 (d, $J=14.3$ Hz; CH_2); 30.7 (d, $J=10.7$ Hz; CH_2); 30.9 (d, $J=4.0$ Hz; CH_2); 31.9 (s, CH_2); 32.3 (d, $J=20.9$ Hz; C_{ipso}-cyclohexyl); 34.6 (d, $J=25.5$ Hz; C_{ipso}-cyclohexyl); 72.2 (s, Cp); 75.3 (d, $J=59.0$ Hz; α-CH); 92.5 (d, $J=7.3$ Hz; β-C); 96.0 (d, $J=6.0$ Hz; β-C); 106.5 (dd, $J=17.1$ Hz, $J=60.3$ Hz; α-C); $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): $\delta=-80.2$ (d, $J=6.0$ Hz; cycl. P); 10.5 (d, $J=6.0$ Hz; PCy_2); MS: $m/z=456$ (M^+, 20%); 259 ($[M-PCy_2]^+$, 100%); $C_{25}H_{38}P_2{}^{56}Fe$: calcd 456.179815; found 456.180006 (HRMS).

***E*–*Z* isomerization of cation 7**: Alcohol **2a** (ca. 40 mg) was dissolved in CD_2Cl_2 in a NMR tube and cooled to -78°C. HBF_4 was then added and the NMR tube was carefully shaken in order to avoid warming. The tube was quickly inserted into the precooled NMR magnet (32 MHz). At -40°C the cation (E)-**7** showed a ^{31}P resonance of $\delta=-34.6$. Over a period of 1 h, a second resonance (corresponding to (Z)-**7**) appeared at $\delta=-34.2$, at the expense of the first signal. After 2 h, the resonance at $\delta=-34.6$ had disappeared completely. (Z)-**7**: ^1H NMR (500 MHz, CD_2Cl_2): $\delta=1.76$ (s, 3H; 3-CH_3); 2.15 (d, $J=6.7$ Hz, 3H; fulvene-CH_3); 2.35 (s, 3H; 4-CH_3); 4.99 (s, 5H; Cp); 6.16 (d, $J=35.4$ Hz, 1H; P=CH); 6.98 (m, 1H; fulvene-H).

[5b·Mo(CO)$_4$] (10): A solution in THF of **5b** (216 mg, 0.49 mmol) was added to (norbornadiene)tetracarbonylmolybdenum (147 mg, 0.49 mmol), also in THF. The mixture was stirred for 30 min at room temperature and then refluxed for 2 h. After filtration over Al_2O_3 the solvent was evaporated to yield **10** as an orange solid in quantitative yield. Recrystallization from ether/hexane afforded orange needles of **10** (124 mg, 0.19 mmol, 40%). ^1H NMR (500 MHz, $CDCl_3$): $\delta=0.85$ (dd, $J=8.0$, 16.0 Hz, 3H; CH_3); 2.28 (s, 3H; CH_3); 2.40 (s, 3H; CH_3); 2.98 (m, 1H; CH); 3.58 (d, $J=32.0$ Hz, 1H; P=CH); 4.35 (s, 5H; Cp); 6.80–7.70 (m, 10H; phenyl-H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta=14.9$ (d, $J=3.7$ Hz; CH_3); 16.9 (s, CH_3); 23.0 (d, $J=7.8$ Hz; CH_3); 30.9 (dd, $J=22.1$, 23.2 Hz; CH); 65.6 (d, $J=17.8$ Hz; α-CH); 73.3 (s, 5C; Cp); 90.4 (d, $J=8.0$ Hz; β-C); 92.1 (s, β-C); 104.7 (d, $J=31.5$ Hz; α-C); 127.3 (s, CH); 128.1 (s, CH); 128.3 (s, CH); 129.5 (s, CH); 129.6 (s, CH); 130.6 (s, CH); 134.4 (s, CH); 134.6 (d, $J=26.0$ Hz; C_{ipso}); 140.9 (d, $J=31.6$ Hz; C_{ipso}); 205.7 (dd, $J=12$, 12 Hz; CO); 210.6 (dd, $J=12$, 15 Hz; CO); 216.5 (dd, $J=10$, 25 Hz; CO); 217.0 (dd, $J=10$, 18 Hz; CO); $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): $\delta=-0.5$ (d, $J=7.1$ Hz; cycl. P); 79.7 (d, $J=7.1$ Hz; PPh_2); IR (THF): $\tilde{\nu}=1886$ (m), 1904 (s), 2024 (m) cm^{-1}; MS: $m/z=654$ (M^+, 50%); 596 ($[M-2CO]^+$, 100%); 568 ($[M-3CO]^+$, 15%); 540 ($[M-4CO]^+$, 40%); $C_{29}H_{26}P_2O_4FeMo$ (652.3): calcd C 53.40, H 4.02; found C 53.13, H 3.84.

[6b·Mo(CO)$_4$] (11): (Norbornadiene)tetracarbonylmolybdenum (147 mg, 0.49 mmol) and **6b** (218 mg, 0.49 mmol) were allowed to react as described above in the synthesis of **10** to give **11** (80 mg, 0.12 mmol, 24%) as orange crystals suitable for X-ray diffraction. ^1H NMR (500 MHz, $CDCl_3$): $\delta=0.87$–2.25 (m, 22H; cyclohexyl-H); 1.00 (m, 3H; CH_3); 1.74 (s, 3H; CH_3); 1.80 (s, 3H; CH_3); 2.12 (m, 1H; CH); 3.00 (d, $J=32.6$ Hz, 1H; P=CH); 4.00 (s, 5H; Cp); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta=14.5$ (s, CH_3); 16.8 (s, CH_3); 23.6 (s, CH_3); 26.3 (d, $J=25.7$ Hz; CH); 26.7 (s, CH_2); 26.9 (s, CH_2); 27.1 (s, CH_2); 27.5 (s, CH_2); 27.6 (d, $J=9.8$ Hz; CH_2); 27.9 (d, $J=10.6$ Hz; CH_2); 28.0 (s, CH_2); 28.9 (s, CH_2); 29.3 (s, CH_2); 30.6 (s, CH_2); 37.3 (d, $J=10.0$ Hz; C_{ipso}-cyclohexyl); 38.1 (d, $J=12.2$ Hz; C_{ipso}-cyclohexyl); 65.0 (d, $J=21.1$ Hz; α-CH); 73.0 (s, Cp); 90.0 (d, $J=11.7$ Hz; α-C); 91.6 (s, β-C); 106.2 (d, $J=29.8$ Hz; β-C); 209.4 (dd, $J=8.0$, 10.0 Hz; CO); 210.5 (dd, $J=12.0$, 13.0 Hz; CO); 216.9 (dd, $J=12.0$, 18.0 Hz; CO); 217.5 (dd, $J=30.0$, 12.0 Hz; CO); $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): $\delta=3.3$ (s, cycl. P); 91.2 (s, PCy_2); IR (THF): $\tilde{\nu}=1880$ (m), 1896 (s), 2016 (m) cm^{-1}; MS: $m/z=666$ (M^+, 20%), 638 ($[M-CO]^+$, 20%), 610 ($[M-2CO]^+$, 20%); $C_{29}H_{38}P_2O_4FeMo$ (664.4): calcd C 52.43, H 5.7; found C 52.57, H 5.75.

X-ray structural analysis of 11: $C_{29}H_{38}FeMoO_4P_2$, $M=664.4$ g mol^{-1}, monoclinic space group $P2_1/c$ (no. 14), $a=12.933(3)$, $b=10.320(3)$, $c=22.881(6)$ Å, $\beta=92.61(2)$°, $V=3051(2)$ Å^3, $Z=4$, $\rho_{calcd}=1.45$ g cm^{-3}, $\mu(Mo_{K\alpha})=10.10$ cm^{-1}, $F(000)=1368$. ENRAF-Nonius CAD4, $\omega-2\theta$ scan, $Mo_{K\alpha}$ radiation (0.71073 Å), graphite monochromator, 20232 reflections at 298 K with $2\leq\theta\leq40$°, crystal size $0.8\times0.2\times0.2$ mm^3. Structure solution with Patterson methods. Refinement[13] on F_o with anisotropic thermal parameters for all non-hydrogen atoms converged at $R=0.048$, $R_w=0.046$, GOF = 1.371 for 586 parameters and 5979 independent observations with $I>2.0\sigma(I)$. Hydrogen atoms were treated as riding atoms. A final difference Fourier synthesis showed a residual density of 0.81 e Å^{-3} (0.83 Å from Mo). 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-101333. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[1] a) *Ferrocenes* (Eds.: A. Togni, T. Hayashi), VCH, Weinheim, **1995**; b) A. Togni, *New Chiral Ferrocenyl Ligands in Asymmetric Catalysis:*

Applications and Mechanistic Studies in *Organic Synthesis via Organometallics* (Ed.: G. Helmchen), Vieweg, Braunschweig, **1997**.
[2] C. Ganter, L. Brassat, C. Glinsböckel, B. Ganter, *Organometallics* **1997**, *16*, 2862 – 2867.
[3] C. Ganter, L. Brassat, B. Ganter, *Chem. Ber.* **1997**, *130*, 1771 – 1776.
[4] C. Ganter, L. Brassat, B. Ganter, *Tetrahedron Asymmetry* **1997**, *8*, 2607 – 2611.
[5] R. M. G. Roberts, J. Silver, A. S. Wells, *Inorg. Chim. Acta* **1989**, *155*, 197 – 201.
[6] T. Hayashi, T. Mise, M. Fukushima, M. Kagotani, N. Nagashima, Y. Hamada, A. Matsumoto, S. Kawakami, M. Konishi, K. Yamamoto, M. Kumada, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138 – 1151.
[7] a) S. Allenmark, *Tetrahedron. Lett.* **1974**, *4*, 371 – 374; b) G. Wagner, R. Herrmann, in ref. [1a], pp. 173 – 218; c) U. Englert, B. Ganter, M. Käser, E. Klinkhammer, T. Wagner, A. Salzer, *Chem. Eur. J.* **1996**, *2*, 523 – 528.
[8] J. I. Seemann, *Chem. Rev.* **1983**, *83*, 83 – 135.
[9] T. D. Turbitt, W. E. Watts, *J. Chem. Soc. Perkin Trans. 2* **1974**, 177 – 184.
[10] S. Taudien, O. Riant, H. B. Kagan, *Tetrahedron Lett.* **1995**, *36*, 3513 – 3516.
[11] G. de Lauzon, B. Deschamps, J. Fischer, F. Mathey, A. Mitschler, *J. Am. Chem. Soc.* **1980**, *102*, 994 – 1000.
[12] R. M. G. Roberts, A. S. Wells, *Inorg. Chim. Acta* **1986**, *112*, 167 – 170.
[13] MolEN, *An Interactive Structure Solution Procedure*, Enraf – Nonius, Delft (The Netherlands), **1990**.

  0947-6539/98/0411-2153 $ 17.50+.25/0