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Synthesis and Characterization of Novel Aminophosphine Ligands Based on Ferrocenodecaline Backbones

Max Weißenbacher[1], **Thomas Sturm**[1], **Hermann Kalchhauser**[1], **Christoph Kratky**[2], and **Walter Weissensteiner**[1,*]

[1] Institut für Organische Chemie, Universität Wien, A-1090 Wien, Austria
[2] Institut für Chemie, Universität Graz, A-8010 Graz, Austria

Summary. Novel aminophosphine ligands for enantioselective transition metal catalysts based on different ferroceno *cis*- and *trans*-decaline backbones were synthesized and structurally characterized. Their palladium dichloride complexes were tested in the asymmetric *Grignard* cross coupling reaction of vinyl bromide and phenylethyl magnesium chloride, but only very low enantioselectivities were obtained. Steric strain in the aminophosphine ligands causes a severe backbone deformation and in addition leads to a slowed rotation of the respective dimethylamino group as was detected by variable temperature NMR spectroscopy.

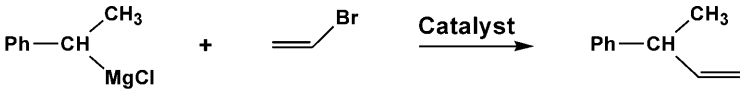
Keywords. Aminophosphines; Asymmetric catalysis; Ferrocene; *Grignard* cross coupling; Variable temperature NMR; X-Ray diffraction.

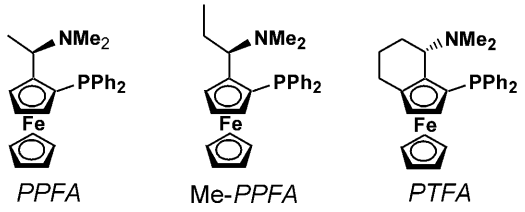
Introduction

Some time ago we have reported the successful application of ferrocenyl aminophosphine *PTFA* (Scheme 1) in enantioselective *Grignard* cross coupling and other catalytic reactions [1]. It is well documented that for this type of catalysts the steric surroundings of the amino functionality are of prime importance [2]. For example, use of *PPFA* in the nickel-catalyzed reaction of phenylethyl magnesium chloride with vinyl bromide gave 3-phenylbutene in 68% *e.e.* as the final product [3], whereas application of its aminopropyl analogue (Me-*PPFA*, Scheme 1) resulted in 86% *e.e.* [4]. Hence, it was of interest to explore analogues of *PTFA* with significantly different steric requirements in close proximity to the dimethylamino group.

We decided to extend the six-membered ring of *PTFA* to a decaline system which, when substituted like *PTFA*, can exist in 4 different structural variations, two with a *cis*- and two with a *trans*-decaline configuration (Scheme 2, **A**–**D**). Such systems are expected to be rather rigid and conformationally less flexible than *PTFA* itself, providing different steric arrangements around the dimethylamino

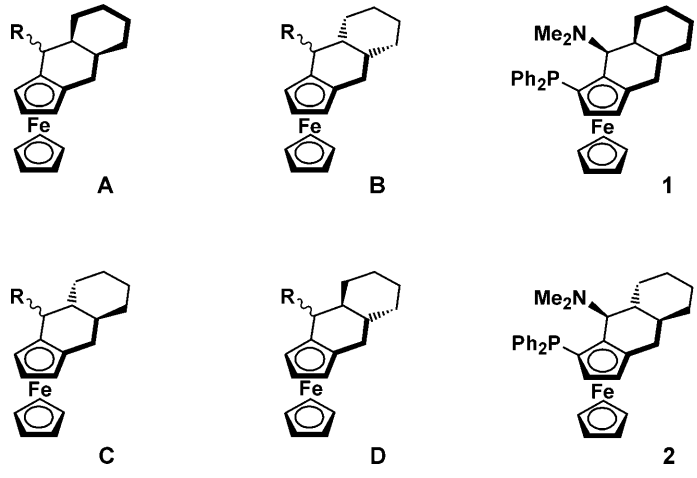
* Corresponding author. E-mail: walter.weissensteiner@univie.ac.at





Catalyst	*e.e.*
$NiCl_2$/*PPFA*	68%
$NiCl_2$/Me-*PPFA*	86%
$PdCl_2$/*PTFA*	79%

Scheme 1



Scheme 2

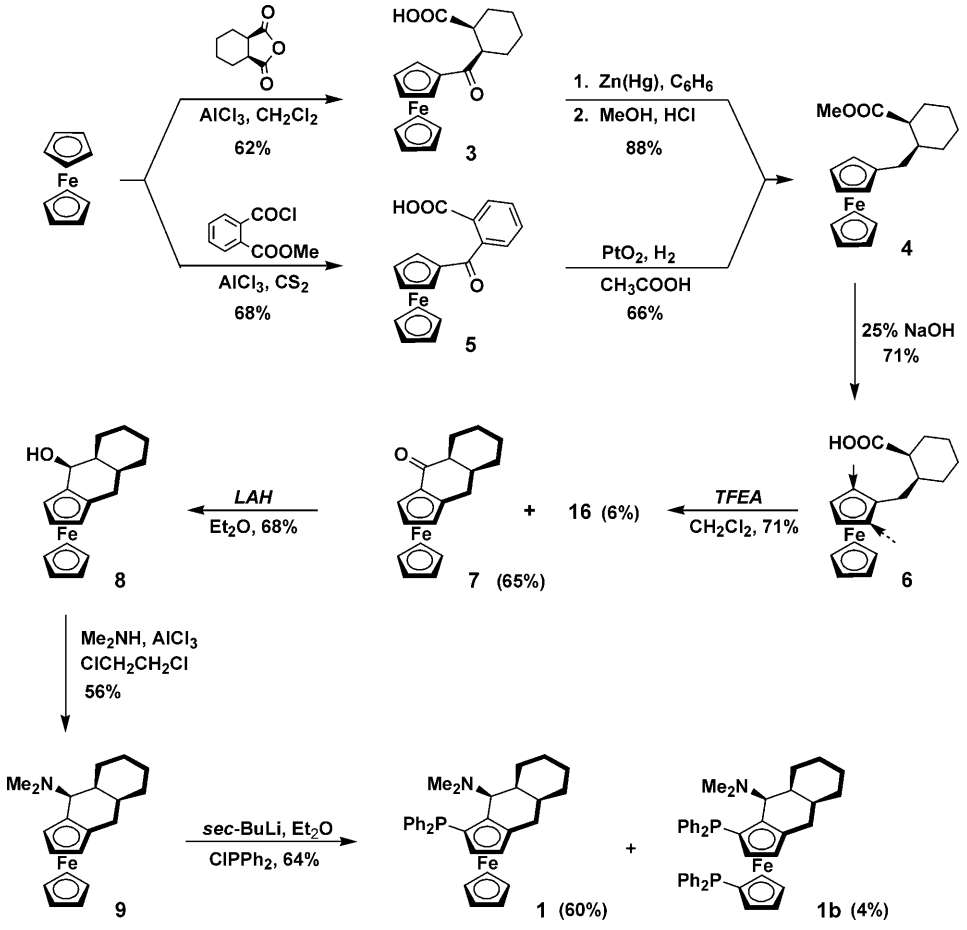
functionality. We now describe synthesis routes to ferrocenyl aminophosphines **1** and **2** and their palladium dichloride complexes **1** · $PdCl_2$ and **2** · $PdCl_2$ with either a *cis* (**1**) or a *trans* (**2**) ferrocenodecaline backbone (Scheme 2), their structural properties, and some catalytic cross coupling experiments.

In the first part, routes to different ferrocenodecaline systems are discussed. In the second part, a diastereoselective synthesis of enantiopure **1** and **2**, starting from a commercially available enantiopure cyclohexenedicarboxylic acid derivative, is described.

Results and Discussion

Synthesis of racemic ligands **1** *and* **2**

Racemic **1** was prepared *via* a seven-step synthesis (Scheme 3) starting from ferrocene which was reacted with *cis*-cyclohexane-1,2-dicarboxylic acid anhydride and $AlCl_3$ in CS_2 giving the ketoacid **3** in 62% yield. **3** was transformed in a *Clemmensen* reduction to the methyl ester of 2-ferrocenylmethyl cyclohexanecarboxylic acid **4** in

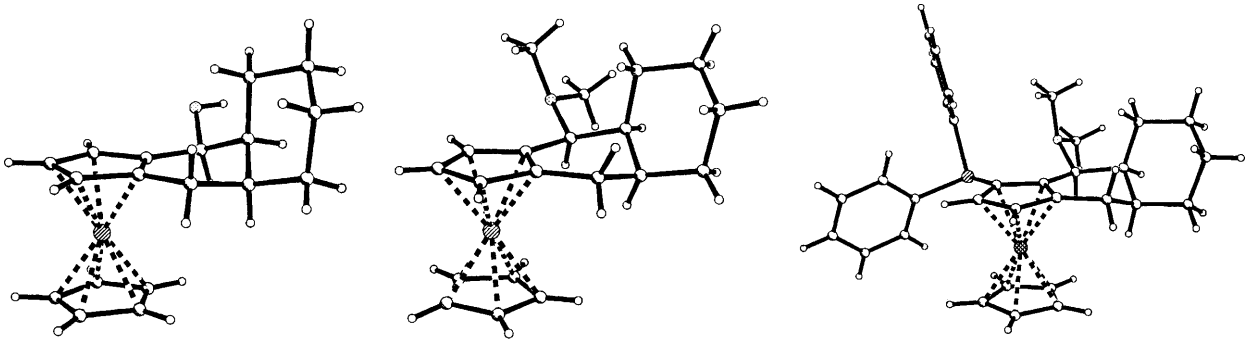


Scheme 3

88% yield. This ester is also accessible *via* catalytic hydrogenation of **5** in acetic acid (PtO_2, 66%). Saponification of **4** led to a mixture of 2-ferrocenylmethyl-cyclohexanecarboxylic acid **6** and a small amount of by-product **15** in an overall yield of 71%. Cyclization with trifluoroacetic anhydride (*TFEA*) afforded 71% of a mixture of two ketones which could be separated by chromatography on silica giving *cis*-ketone **7** as the major product (65%) and *trans*-ketone **16** as a by-product (6%).

Interestingly, the cyclization of acid **6** gave *trans*-ketone **16** as the by-product instead of the second *cis*-ketone of type **B** (Scheme 2) which, beside **7**, was expected to be formed in this ring closure reaction (see Scheme 3, **6** → **7**, dotted arrow), indicating a partial epimerization of ester **4** in the saponification step leading to acid **15** as the by-product which functions as the precursor of ketone **16** (see below).

Reduction of **7** with either $LiAlH_4$ in Et_2O or B_2H_6 in *THF* resulted in *exo*-alcohol **8** whose stereochemical integrity was proved by a crystal structure analysis (Fig. 1) confirming the *cis*-configuration of the decaline system (Scheme 2, type **A**) as well as the *exo*-position of the hydroxyl group [5]. For the structural characterization of ketone **16**, see below.

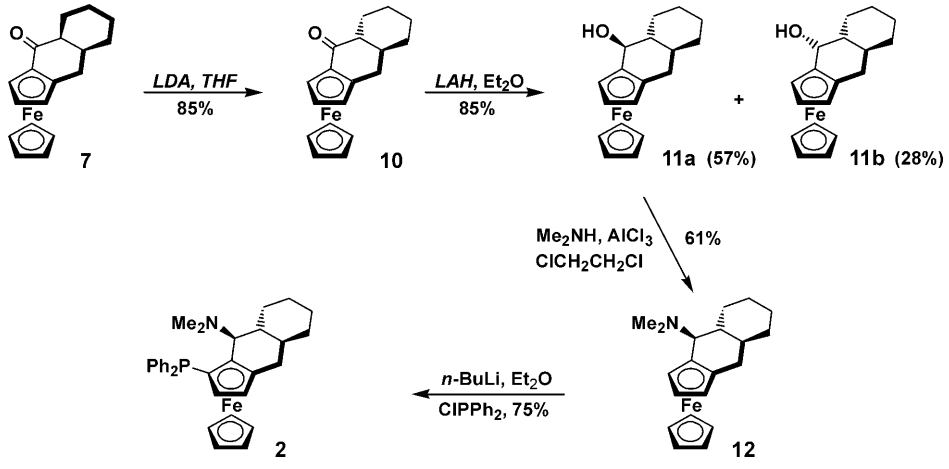


8 **9** **1**

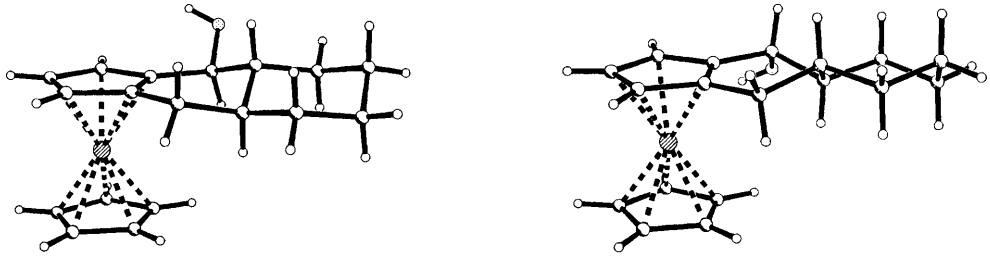
Fig. 1. Molecular structures of **8**, **9**, and **1**

Further reaction of alcohol **8** with $(CH_3)_2NH/AlCl_3$ in 1,2-dichloroethane gave amine **9** with retention of configuration as was confirmed by X-ray diffraction (Fig. 1) [6]. Finally, treatment of **9** with *sec*-BuLi in Et_2O and quenching with $ClPPh_2$ led to aminophosphine **1** (60%) and to aminodiphosphine **1b** (4%). It is important to note that the lithiation step is especially sensitive to the concentration of amine **9** as well as to the choice of solvent and the reaction temperature. Acceptable yields could only be achieved at high amine concentrations in diethyl ether. The molecular structure of **1** was determined by X-ray diffraction and is shown in Fig. 1.

Racemic aminophosphine **2** with a *trans*-decaline backbone was accessible from ketone **7** in 4 steps (Scheme 4). Epimerization of **7** with *LDA* in *THF* led to ketone **10** in 85% yield. Subsequent reduction with $LiAlH_4$ in Et_2O resulted in a mixture of alcohols **11a** (57%) and **11b** (28%) which could be separated by chromatography on silica. An X-ray diffraction study of **11a** confirmed the *trans*-configuration of the decaline system as well as the *exo*-position of the hydroxyl group (Fig. 2). Reaction of **11a** with $(CH_3)_2NH/AlCl_3$ in 1,2-dichloroethane afforded



Scheme 4



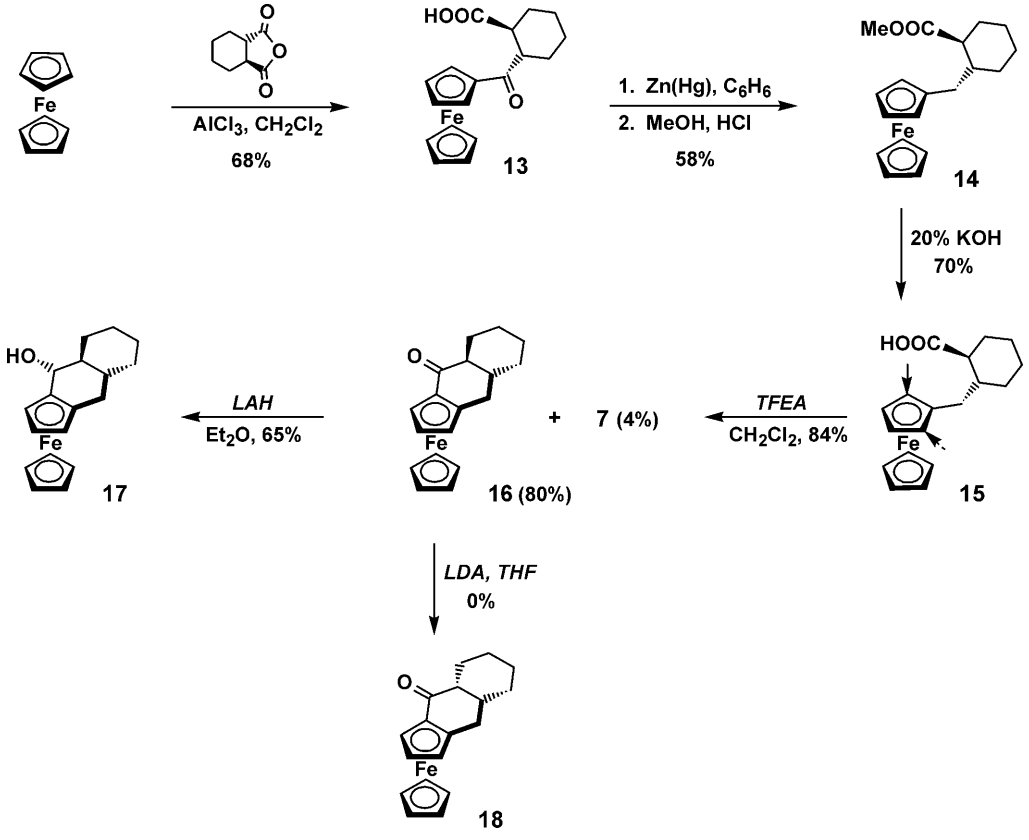
11a **17**

Fig. 2. Molecular structures of **11a** and **17**

exo-amine **12** under retention of configuration; *ortho*-lithiation of **12** with *n*-BuLi in Et_2O and quenching with $ClPPh_2$ yielded aminophosphine **2** (75%).

A synthesis route to derivatives with a *trans*-ferrocenodecaline backbone of type **D** (Scheme 2) starts – in analogy to the synthesis of **1** – from ferrocene and *trans*-cyclohexanedicarboxylic acid anhydride which, when reacted with $AlCl_3$ in CH_2Cl_2, gave ketoacid **13** in 68% yield (Scheme 5).

Clemmensen reduction and esterification of **13** led to the methyl ester **14** (58%) which after saponification (**15**, 70%) and cyclization with *TFEA* resulted in a



Scheme 5

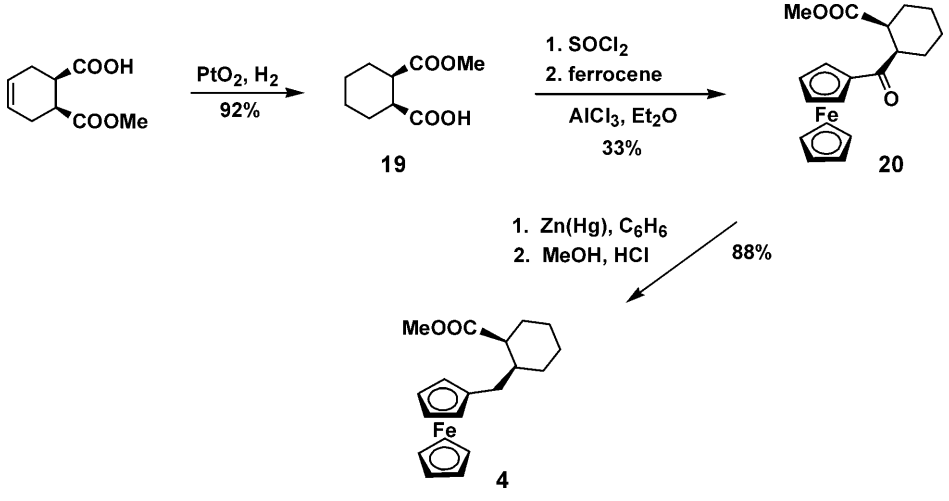
mixture of ketones which could be separated on silica, the *trans*-ketone **16** (80%) being the major and the *cis*-ketone **7** (4%) being the minor product. The formation of **7** is again the result of a partial epimerization in the saponification step of **14**. As before, the cyclization of **15** to **16** is a highly diastereoselective reaction. Reduction of **16** with $LiAlH_4$ in Et_2O gave exclusively *endo*-alcohol **17** whose structure was elucidated by an X-ray diffraction study confirming both the *trans*-decaline backbone of type **D** and the *endo*-position of the hydroxyl group (Fig. 2). In this particular case, all attempts to transform either the keto group of **16** or the hydroxyl group of **17** into an amino functionality failed.

In principle, like in the synthesis of *trans*-**2** from *cis*-**7** (Scheme 4), epimerization of *trans*-ketone **16** could lead to the corresponding *cis*-ketone **18** with a decaline system of type **B** (Scheme 2). However, it was not possible to isolate such a *cis*-ketone from the reaction mixture when **16** was treated with *LDA* in *THF*.

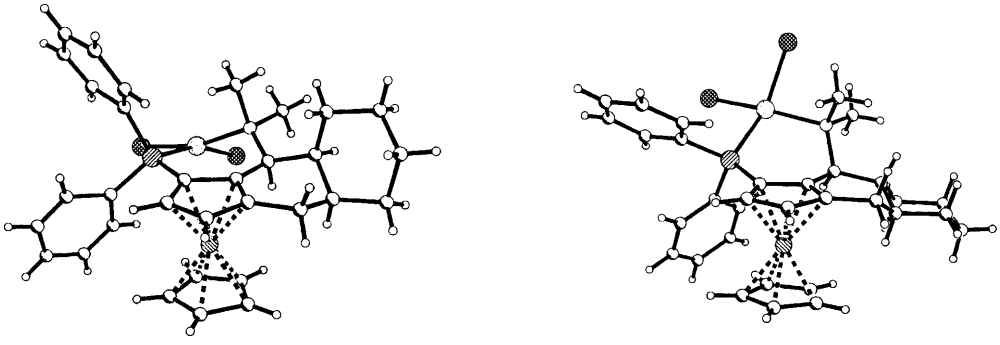
Synthesis of enantiopure ligands **1** *and* **2**

In analogy to one of the preparation methods of *PTFA* [7] it was tried to separate racemic ketones **7** and **10** by chromatography on chiral stationary phases such as triacetyl or tribenzoyl cellulose. However, only on Chiralcel OD type stationary phases reasonable separations could be achieved. Hence, a diastereoselective route for the synthesis of ketone **7**, the precursor of both aminophosphines **1** and **2**, was established.

Commercially available enantiopure *cis*-1,2-cyclohexenedicarboxylic acid monomethylester was catalytically hydrogenated to the corresponding cyclohexane derivative **19** in 92% yield (Scheme 6). Treatment with $SOCl_2$ and reaction with ferrocene gave 33% of enantiopure ketoester **20**. *Clemmensen* reduction led to ester **4** (88%) which finally was transformed into the key intermediate **7** following the preparation method for **1** as described above (Scheme 3). The enantiomeric purity of **7** (as well as those of **10** and **16**) could be confirmed by HPLC on Chiralcel OD. It is interesting to note that the enantiopure ester **4** does not show any detectable



Scheme 6



1·$PdCl_2$ **2**·$PdCl_2$

Fig. 3. Molecular structures of **1** · $PdCl_2$ and **2** · $PdCl_2$

specific rotation, neither at 589 nor at 578 nm. Only in the CD spectrum transitions of small intensity were observed. The synthesis of enantiopure ligand continues exactly as described for the racemic ligand (Schemes 2 and 3).

Synthesis of palladium dichloride complexes **1** · $PdCl_2$ *and* **2** · $PdCl_2$

Racemic as well as enantiomerically pure **1** · $PdCl_2$ and **2** · $PdCl_2$ are accessible by reacting ligands **1** or **2** with $(CH_3CN)_2PdCl_2$ in benzene in 86 and 64% yield, respectively. The molecular structures of both *rac*-**1** · $PdCl_2$ and *rac*-**2** · $PdCl_2$ were determined (Fig. 3).

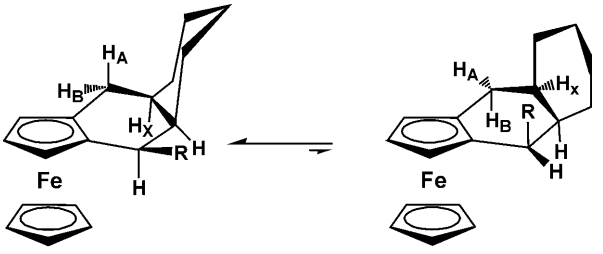
As mentioned above, the cyclization reactions of acid **6** to ketone **7** as well as of acid **15** to ketone **16** are highly diastereoselective. As indicated in Schemes 3 and 5, in each case two diastereomers are expected to be formed, but only **7** and **16** could be isolated. Force field calculations [8] including all 4 possible diastereomeric ketones (Scheme 2, *R*=O=) suggest that the cyclization reactions are likely to be kinetically controlled since ketones of type **A** (**7**) and **B** (**18**) (possible reaction products from **6**) as well as ketones of type **C** (**16**) and **D** (**10**) (possible reaction products of **15**) differ in ground state energy only by 0.6 kJ/mol (energy differences to the minimum energy structure of **16**: **10**: 0.6 kJ/mol, **7**: 11.0 kJ/mol, **18**: 11.6 kJ/mol). According to these calculations, the *trans*-ketones **10** and **16** are significantly more stable than their *cis*-diastereomers **7** and **18** (10.4 and 11.6 kJ/mol, respectively), thus allowing to rationalize the fact that *LDA* epimerizes *cis*-ketone **7** to the more stable *trans*-ketone **10**, but not *trans*-**16** to the less stable *cis*-**18**.

Structural features of **1** · $PdCl_2$ *and its precursors* **8**, **9**, *and* **1**

The molecular structures of **8**, **9**, **1** (Fig. 1), and **1** · $PdCl_2$ (Fig. 3) in the solid state were determined by single crystal X-ray diffraction; the corresponding data are given in Table 1. The general features of these 4 derivatives are rather similar: the ferrocenodecaline backbone of type **A** (Scheme 7) adopts one of two interconvertible structures with the annelated six-membered ring system in a chair conformation and with the *exo*-substituents (–OH or $–NMe_2$) in a *pseudo*-equatorial position

Table 1. Crystallographic data of compounds **1**, **1** · $PdCl_2$, **2** · $PdCl_2$, **8**, **9**, **11a**, and **17**

	1	**1** · $PdCl_2$	**2** · $PdCl_2$	**8**	**9**	**11a**	**17**
Formula	$C_{32}H_{36}FeNP$	$C_{32}H_{36}NPFePdCl_2$	$C_{32}H_{36}NPFePdCl_2$	$C_{18}H_{22}FeO$	$C_{20}H_{27}FeN$	$C_{18}H_{22}FeO$	$C_{18}H_{22}FeO$
Solvent of crystallization	–	CH_2Cl_2	CH_2Cl_2	–	–	$(C_2H_5OH)_{1/2}$	–
Formula weight	521.44	738.75	738.75	310.21	337.28	333.24	310.21
T/K	98	298	98	298	298	100	298
Space group	Pbca	$P2_1/c$	$P2_1/n$	P-3	$P2_1/c$	P-1	P-1
Cell dimensions: a/Å	9.072(2)	17.409(12)	15.527(3)	28.175(4)	13.980(2)	10.458(2)	6.865(2)
b/Å	15.851(3)	15.681(11)	9.735(2)	28.175(4)	10.647(2)	11.802(2)	10.968(2)
c/Å	36.430(7)	25.491(18)	22.388(4)	10.225(2)	11.535(3)	15.390(3)	11.273(2)
α/°	90	90	90	90	90	102.36(3)	61.98(3)
β/°	90	107.37(5)	108.89(3)	90	92.48(3)	96.81(3)	76.89(3)
γ/°	90	90	90	120	90	114.42(3)	85.30(3)
V/Å^3	5239(2)	6642(8)	3202(2)	7030(2)	1715(1)	1643(1)	729(1)
Z	8	8	4	18	4	4	2
d_x/Mg · m^{-3}	1.322	1.567	1.626	1.319	1.306	1.347	1.412
μ_{calc}/mm^{-1}	0.658	1.37	1.42	0.959	0.876	0.918	1.026
F(000)	2208	3184	1592	2952	720	708	328
Data collection							
θ-range/°	2.8–22.5	2.8–20.0	2.8–30.34	2.9–25.0	2.9–20.0	2.9–30.0	3.0–25.0
Limiting indices: h	$-9 \le h \le 8$	$-16 \le h \le 16$	$-21 \le h \le 20$	$-33 \le h \le 32$	$-13 \le h \le 1$	$-14 \le h \le 14$	$-3 \le h \le 8$
k	$-4 \le k \le 16$	$-15 \le k \le 15$	$-1 \le k \le 13$	$-33 \le k \le 33$	$-10 \le k \le 10$	$-16 \le k \le 16$	$-11 \le k \le 11$
l	$2 \le l \le 39$	$-24 \le l \le 24$	$-1 \le l \le 31$	$-5 \le l \le 12$	$-10 \le l \le 11$	$-1 \le l \le 21$	$-12 \le l \le 11$
Reflections collected	5497	7228	11123	26264	1631	10554	2307
Independent reflections	3267	6094	9468	8282	1311	9566	1979
R(int)	0.0375	0.153	0.094	0.077	0.041	0.038	0.047
Refinement							
Data/parameters	3261/316	6048/739	9413/371	8282/541	1311/207	9534/388	1979/181
R_1/wR_2 for $I > 2\sigma(I)$	0.036/0.091	0.123/0.265	0.169/0.411	0.059/0.159	0.060/0.173	0.062/0.166	0.044/0.147
R_1/wR_2 for all data	0.045/0.105	0.245/0.352	0.210/0.445	0.083/0.174	0.065/0.183	0.116/0.218	0.049/0.153
Max. diff. peak/eÅ^{-3}	0.347	0.994	5.541	1.667	0.465	1.762	0.467



A-*eq* **B**-αx

Scheme 7

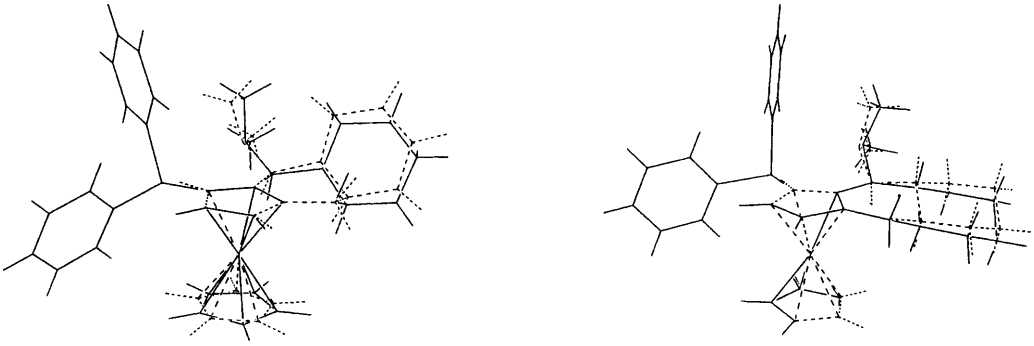


Fig. 4. Superposition of the molecular structures of **9** and **1** (left) and of the calculated structures of **12** and **2** (right)

(**A**-*eq*). The molecular structure of aminophosphine **1** is of particular interest since both functional groups are well pre-organized for the formation of a chelate complex, the amino and the phosphino lone pairs pointing almost towards each other. A comparison of amine **9** and aminophosphine **1** shows that the phosphino group obviously imposes severe steric strain on the system which is released by tilting the ferrocene against the decaline unit (Fig. 4).

According to a simple analysis of the vicinal coupling constants $J(H_AH_X)$ and $J(H_BH_X)$ (Scheme 7), the predominant conformation of **8**, **9**, **1**, and **1** · $PdCl_2$ in solution is identical to that found in the solid state (for coupling constant values, see Experimental). The effect of strain in aminophosphine **1** can also be observed in solution by variable temperature ^{1}H NMR spectroscopy: upon lowering the temperature, an exchange phenomenon involving the dimethylamino group is observed (for details, see below).

Structural features of **2** · $PdCl_2$*, its precursors* **11a**, **12**, *and* **2**, *and alcohol* **17**

Both ferroceno *trans*-decaline systems (types **C** and **D**, Scheme 2), represented *e.g.* by alcohols **11** and **17** (Fig. 2), can adopt only one single conformation with a chair-like annelated six-membered ring. Force field calculations on **11**, **12**, and **2** showed that, in agreement with the crystal structures of **11a** and **2** · $PdCl_2$, the *exo*-equatorial position of the hydroxyl or dimethylamino substituent is energetically

either slightly (0.6 kJ/mol, **11a**) or strongly (19.7 kJ/mol, **12**; 24.7 kJ/mol, **2**) preferred over the *endo*-axial arrangement. Some structural properties are similar to those of their *cis*-analogues **9** and **1**. Again, steric strain in aminophosphine **2** leads to a strong tilt of the decaline system relative to the ferrocene unit (Fig. 4). Like in **1**, the functional groups are well pre-organized for chelate formation.

Dynamic processes in **1** *and* **2**

Variable temperature ^{1}H NMR measurements of **1** and **2** in toluene-d_8 were carried out. In both cases, the room temperature spectra show a rather broad singulet for the dimethylamino group which decoalesces upon lowering the temperature (T_c: 302 ± 2 K (**1**), 270 ± 5 K (**2**)), finally leading to two singulets at the slow exchange limit at 210 K ($\Delta\nu$: 12.5 Hz (**1**), 600 Hz (**2**)). The observed exchange phenomena are interpreted as being caused by a slowed rotation of the dimethylamino unit about the C–NMe_2 bond. The activation barrier of this process was calculated as 65.8 ± 2.1 kJ/mol for **1** and 49.9 ± 2.1 kJ/mol for **2**, respectively; the modified *Eyring* equation ($\Delta G^{\neq} = 4.57 T_c \times (9.97 + \log T_c/\Delta\nu)$; T_c: coalescence temperature, $\Delta\nu$: shift difference at the slow exchange limit) was used. A higher barrier for *cis*-decaline **1** as compared to that of *trans*-oriented **2** fits the expectations.

Catalytic reactions

Complexes (+)-(4*S*,4a*S*,8a*S*,R_m)-**1** · $PdCl_2$ and (−)-(4*S*,4a*R*,8a*S*,R_m)-**2** · $PdCl_2$ were tested in the standard *Grignard* cross coupling reaction of vinyl bromide and phenylethyl magnesium chloride (Scheme 1). In each case, high chemical yields (**1** · $PdCl_2$: 96%; **2** · $PdCl_2$: 84% based on vinyl bromide) were obtained, but nearly racemic product 3-phenyl-but-1-ene was isolated (**1** · $PdCl_2$: 4% *e.e.*; **2** · $PdCl_2$: 1% *e.e.*). This result strongly contrasts the 79% *e.e.* obtained with (4*R*, R_m)-(4-*N*,*N*-dimethylamino-3-diphenylphosphino-(η^5-4,5,6,7-tetrahydro-indenyl))-(η^5-cyclopenta-dienyl)-iron(II), (*R*, R_m)-*PTFA* ([1a], Scheme 1). Possible structural reasons could be either the rather strained ferrocenodecaline backbones of **1** · $PdCl_2$ and **2** · $PdCl_2$ (see above) or, more likely, the fact that in *PTFA* the dimethylamino group is located in the *endo*-, in **1** · $PdCl_2$ and **2** · $PdCl_2$ in the *exo*-position. Although obviously **1** · $PdCl_2$ and **2** · $PdCl_2$ are performing poorly in *Grignard* cross coupling reactions, they seem to be interesting candidates for allylic alkylation and amination reactions.

Experimental

General

NMR spectra were recorded on a Bruker AM-400 spectrometer in $CDCl_3$ unless stated otherwise (^{1}H: 400.0, ^{13}C: 100.6, ^{31}P: 161.9 MHz). Chemical shifts are given relative to internal *TMS* (^{1}H and ^{13}C NMR) or external 85% H_3PO_4 (^{31}P NMR). The coupling constants given for ^{13}C spectra refer to ^{13}C,^{31}P-couplings. Melting points were determined on a Kofler melting point apparatus and are uncorrected. Mass spectra were recorded on a Varian MAT-CH 7 spectrometer, CD spectra on a Jobin Yvon CD 6 dichrograph. Optical rotations were measured on a Perkin Elmer 241 polarimeter. For analytical HPLC, a Hewlett Packard HP1090 liquid chromatograph was used. The enantiomeric purity

of ketones **7**, **10**, and **16** was determined by HPLC on Chiralcel OD (Daicel); separation conditions: flow 0.5 cm^3/min, column temperature 35°C, eluent hexane:isopropanol = 95:5, $c = 2$ mg/cm^3, injected 1 mm^3. Elemental analyses were carried out at the *Mikroanalytisches Laboratorium der Universität Wien*; the results agreed favourably with the theoretical values. Reactions under inert atmosphere (Ar) were carried out using standard *Schlenk* techniques. All solvents were dried by standard procedures before use.

(4S,4aS,8aS,R_m)-(4-N,N-Dimethylamino-3-diphenylphosphino-(η^5-5,6,7,8-tetrahydro-4H,9H-benz[f]indenyl))-(η^5-cyclopentadienyl)-iron(II) (**1**; $C_{32}H_{36}FeNP$)

To a degassed solution of 0.5 g (1.5 mmol) of **9** in 2 cm^3 of diethyl ether, 1.5 cm^3 (2.4 mmol) of *n*-BuLi (1.6 *M* in hexane) were added at 0°C. After stirring for 18 h at room temperature, 0.52 cm^3 (2.9 mmol) of chlorodiphenylphosphine were added at −10°C, and the reaction mixture was stirred for additional 5 h at room temperature. After hydrolysis with 5 cm^3 of saturated $NaHCO_3$ solution the organic layer was separated, diluted with 15 cm^3 of diethyl ether, and washed with H_2O (2 × 10 cm^3). After drying over $MgSO_4$ and removal of the solvent, the crude product was chromatographed on silica (petrol ether:triethylamine = 97:3) to yield 0.46 g (0.9 mmol, 60%) of **1**.

M.p.: 161–165°C; ^{1}H NMR: $\delta = 1.04$–1.17 (m, 2H), 1.27–1.43 (m, 3H), 1.49–1.70 (m, 3H), 1.73–1.92 (bs, 6H), 2.10 (H_B), 2.57 (H_A, AB, $J_{AB} = 13.7$ Hz, $J_{AX} = 12.3$ Hz, $J_{BX} = 2.9$ Hz, 2H), 2.31 (m, 1H), 2.47–2.54 (m, 1H), 3.69 (s, 5H), 3.82 (m, 1H), 4.20 (m, 1H), 4.57 (d, $J = 7.4$ Hz, 1H), 7.10–7.19 (m, 3H), 7.21–7.29 (m, 3H), 7.36–7.44 (m, 2H), 7.58–7.66 (m, 2H) ppm; ^{13}C NMR: $\delta = 20.96$ (CH_2), 23.56 (CH_2), 25.01 (CH_2), 26.84 (CH_2), 32.04 (CH_2), 34.60 (CH), 40.99 ($N(CH_3)_2$), 41.88 (CH), 63.31 (CH), 67.38 (*Cp*), 70.48 (d, $J = 5.3$ Hz, *Cp*), 71.26 (*Cp*), 72.04 (d, $J = 11.5$ Hz, *Cp*), 89.58 (d, $J = 4.6$ Hz, *Cp*), 92.85 (d, $J = 21.4$ Hz, *Cp*), 127.63 (d, $J = 7.6$ Hz, 4Ph), 127.66 (Ph), 128.34 (Ph), 133.20 (d, $J = 21.4$ Hz, 2Ph), 135.17 (d, $J = 22.9$ Hz, 2Ph), 139.84 (d, $J = 12.2$ Hz, Ph), 140.91 (d $J = 11.4$ Hz, Ph) ppm; MS: m/z (%) = 521 (47, M^+), 478 (36), 292 (35), 242 (50), 199 (100), 185 (54), 149 (33), 121 (15), 108 (37), 91 (25); $[\alpha]^{20}$ (nm) = +49.3 (589), +52.4 (578)° ($c = 0.87$, $CHCl_3$).

(4S,4aS,8aS,R_m)-((4-N,N-Dimethylamino-3-diphenylphosphino-(η^5-5,6,7,8-tetrahydro-4H,9H-benz[f]indenyl))-(η^5-cyclopentadienyl)-iron(II))-$PdCl_2$ (**1** · $PdCl_2$; $C_{32}H_{36}Cl_2FeNPPd$)

To a degassed suspension of 36 mg (0.14 mmol) of bisacetonitrilo palladium dichloride in 2.5 cm^3 of benzene, a degassed solution of 80 mg (0.15 mmol) of **1** in 2 cm^3 of benzene was added, and the reaction mixture was stirred at room temperature for 24 h. The precipitate was filtered off and washed with diethyl ether to yield 83 mg (0.12 mmol, 86%) of **1** · $PdCl_2$.

M.p.: decomposition above 160°C; ^{1}H NMR: $\delta = 1.10$–1.34 (m, 2H), 1.35–1.77 (m, 6H), 2.35 (m, 1H), 2.44 (d, $J(^1H,^{31}P) = 4.9$ Hz, 3H), 2.48 (m, 2H), 2.79 (dd, $J_{AB} = 17.8$ Hz, $J_{AX} = 13.7$ Hz, H_A), 3.26 (s, 3H), 3.95 (s, 5H), 4.06 (m, 1H), 4.56 (d, $J = 2.5$ Hz, 1H), 4.87 (d, $J = 5.4$ Hz, 1H), 7.31–7.48 (m, 6H), 7.77–7.94 (m, 4H) ppm; ^{13}C NMR: $\delta = 19.77$ (CH_2), 22.60 (CH_2), 24.70 (CH_2), 25.67 (CH_2), 31.18 (CH_2), 34.05 (CH), 39.89 (CH), 50.72 (d, $J = 5.3$ Hz, $N(CH_3)$), 53.96 ($N(CH_3)$), 70.57 (d, $J = 6.1$ Hz, *Cp*), 70.71, 71.76, 72.92 (*Cp*), 88.17 (d, $J = 29.9$ Hz, *Cp*), 89.05 (d, $J = 12.6$ Hz, *Cp*), 127.37 (d, $J = 18.9$ Hz, 2Ph), 128.80 (d, $J = 17.3$ Hz, 2Ph), 130.30 (d, $J = 77.2$ Hz, Ph), 131.06 (2Ph), 131.28 (d, $J = 81.9$ Hz, Ph), 132.72 (d, $J = 15.7$ Hz, 2Ph), 135.51 (d, $J = 17.3$ Hz, 2Ph) ppm; $[\alpha]^{20}$ (nm) = +32.3 (589), +32.3 (578)° ($c = 0.099$, $CHCl_3$).

(4S,4aR,8aS,R_m)-(4-N,N-Dimethylamino-3-diphenylphosphino-(η^5-5,6,7,8-tetrahydro-4H,9H-benz[f]indenyl))-(η^5-cyclopentadienyl)-iron(II) (**2**; $C_{32}H_{36}FeNP$)

To a degassed solution of 500 mg (1.5 mmol) of **12** in 3 cm^3 of diethyl ether, 1.5 cm^3 (2.4 mmol) of *n*-BuLi (1.6 *M* solution in hexane) were added at 0°C. After stirring at room temperature for 20 h, 0.8 cm^3

(4.3 mmol) of chlorodiphenylphosphine were added at 0°C, and the solution was stirred for additional 4.5 h at room temperature and finally quenched with 10 cm^3 of saturated aqueous $NaHCO_3$ solution. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 ($3 \times 10\,cm^3$). The combined organic phases were washed with H_2O ($3 \times 15\,cm^3$) and dried over $MgSO_4$. After evaporation of the solvent the residue was chromatographed on silica (petrol ether:ethylacetate : triethylamine = 79:20:1) to yield 590 mg (1.13 mmol, 76%) of **2**.

M.p.: 57–59°C; ^{1}H NMR: $\delta = 1.0$–1.4 (m, 6H), 1.68–2.1 (m, 11H), 2.3–2.39 (m, 1H), 3.64–3.66 (m, 1H), 3.88 (s, 5H), 3.94 (d, $J = 7.9$ Hz, 1H), 4.13–4.15 (m, 1H), 7.17–7.37 (m, 8H), 7.55–7.61 (m, 2H) ppm; ^{13}C NMR: $\delta = 26.30$ (CH_2), 26.33 (CH_2), 32.70 (CH_2), 34.17 (CH_2), 34.51 (CH_2), 39.76, 40.35, 66.15, 66.28, 69.55, 69.61, 70.69 (*Cp*), 73.66 (d, $J = 30.3$ Hz, *Cp*), 89.76 (d, $J = 15.2$ Hz, *Cp*), 93.12 (d, $J = 75.8$ Hz, *Cp*), 127.3 (Ph), 127.46 (d, $J = 30.3$ Hz, Ph), 127.64 (d, $J = 27.3$ Hz, Ph), 128.20 (Ph), 132.47 (d, $J = 81.9$ Hz, Ph), 134.94 (d, $J = 85.0$ Hz, Ph), 139.56 (d, $J = 48.5$ Hz, Ph), 140.58 (d, $J = 33.4$ Hz, Ph) ppm; MS: m/z (%) = 521.3 (33.4, M^+), 478.3 (35.7), 476.3 (22.6), 292.2 (37.0), 291.2 (28.2), 242.1 (41.6), 200.0 (42.1), 199.0 (100.0), 185.0 (13.4), 183.0 (43.1), 120.8 (13.0), 107.8 (29.7), 106.8 (13.9), 90.8 (19.3); $[\alpha]^{20}$ (nm) = + 38.1 (589), + 40.7 (578)° ($c = 0.425$, $CHCl_3$).

(4S,4aR,8aS,R_m)-((4-N,N-Dimethylamino-3-diphenylphosphino-(η^5-5,6,7,8-tetrahydro-4H,9H-benz[f]indenyl))-(η^5-cyclopentadienyl)-iron(II))-$PdCl_2$ (**2** · $PdCl_2$, $C_{32}H_{36}Cl_2FeNPPd$)

To a degassed suspension of 65 mg (0.26 mmol) of bisacetonitrilo palladium dichloride in 2.5 cm^3 benzene, a solution of 140 mg (0.27 mmol) of **2** in 2.5 cm^3 of benzene was added, and the reaction mixture was stirred at room temperature for 24 h. The precipitate was filtered off and washed with diethyl ether. The product was recrystallized from CH_2Cl_2/hexane to yield 120 mg (0.17 mmol, 64%) of **2** · $PdCl_2$.

M.p.: decomposition above 160°C; ^{1}H NMR: $\delta = 1.20$–1.50 (m, 6H), 1.80–1.92 (m, 3H), 2.01–2.11 (m, 1H), 2.21 (d, $J = 9.4$ Hz, 1H), 2.27 (dd, $J_1 = 14.8$ Hz, $J_2 = 3.4$ Hz, 1H), 2.33 (s, 3H), 3.40 (s, 3H), 3.63 (s, 5H), 4.0–4.03 (m, 1H), 4.19–4.21 (m, 1H), 4.54 (d, $J = 2.5$ Hz, 1H), 7.30–7.36 (m, 2H), 7.41–7.46 (m, 1H), 7.51–7.62 (m, 5H), 8.23–8.30 (m, 2H) ppm; ^{13}C NMR: $\delta = 26.40$ (CH_2), 26.71 (CH_2), 30.06 (CH_2), 34.80 (CH_2), 36.92 (CH_2), 38.13, 41.90, 42.54, 51.40, 69.09 (d, $J = 27.3$ Hz), 70.89 (d, $J = 15.2$ Hz), 71.38 (*Cp*), 71.56 (d, $J = 9.1$ Hz), 87.11, 92.49, 127.83 (d, $J = 48.5$ Hz, Ph), 128.29 (d, $J = 45.5$ Hz, Ph), 130.63 (d, $J = 12.1$ Hz, Ph), 131.48 (d, $J = 45.5$ Hz, Ph), 131.59 (d, $J = 19.7$ Hz, Ph), 132.17 (d, $J = 32.1$ Hz, Ph), 133.73 (d, $J = 36.4$ Hz, Ph), 135.41 (d, $J = 45.5$ Hz, Ph); $[\alpha]^{20}$ (nm) = − 38.8 (589), − 42.8 (578)° ($c = 0.049$, $CHCl_3$); CD (CH_2Cl_2): λ_{max} ($\Delta\varepsilon$) = 273 (+ 0.38), 313 (− 0.22), 376 (+ 0.09), 494 (− 0.08) nm.

Racemic cis-2-ferrocenoyl-cyclohexane-1-carboxylic acid (**3**; $C_{18}H_{20}FeO_3$)

To a suspension of 34.7 g (260 mmol) $AlCl_3$ in 300 cm^3 of CH_2Cl_2, a solution of 44.3 g (240 mmol) ferrocene and 19 g (120 mol) *cis*-cyclohexane-1,2-dicarboxylic acid anhydride in 300 cm^3 CH_2Cl_2 was added within 45 min at room temperature. The reaction mixture was stirred for additional 2 h at room temperature and then poured on ice. The *pH* was adjusted to 4, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 ($4 \times 100\,cm^3$), and the combined organic layers were concentrated to approximately 500 cm^3 and extracted with a 2 *N* aqueous solution of NaOH ($4 \times 250\,cm^3$). Traces of organic solvents were removed from the aqueous phase *in vacuo*, and the product was precipitated by slow addition of phosphoric acid (50%) at 5°C. The dark orange precipitate was filtered off, washed with H_2O, and dried over $CaCl_2$ to yield 25.3 g (74 mmol, 62%) of **3**.

M.p.: 51–54°C; ^{1}H NMR: $\delta = 1.17$–1.53 (m, 3H), 1.66–1.98 (m, 3H), 2.09–2.30 (m, 2H), 2.58 (m, 1H), 3.49 (m, 1H), 4.22 (s, 5H), 4.44 (s, 1H), 4.65 (s, 1H), 4.86 (s, 1H) ppm; ^{13}C NMR: $\delta = 22.80$ (CH_2), 24.39 (CH_2), 25.35 (CH_2), 29.37 (CH_2), 42.68 (CH), 46.43 (CH), 69.09 (*Cp*), 69.94 (*Cp*), 70.24 (*Cp*), 71.81 (*Cp*), 71.94 (*Cp*), 77.81 (*Cp*), 179.68 (CO), 206.79 (CO) ppm; MS: m/z (%) = 340 (94, M^+), 213 (98), 186 (87), 121 (82), 92 (100).

(1S,2R)-2-Ferrocenylmethyl-cyclohexane-1-carboxylic acid methylester (**4**; $C_{19}H_{24}FeO_2$)

Method 1: To a solution of 6.9 g (20.3 mmol) of **3** in 220 cm^3 of MeOH, 35 cm^3 of benzene, 35 cm^3 of H_2O, and 35 cm^3 of concentrated HCl, freshly prepared zinc amalgam was added, and the mixture was refluxed for 24 h. After cooling to room temperature, the amalgam was filtered off and washed with benzene. The organic layer was washed with brine ($2 \times 100\,cm^3$) and dried over $MgSO_4$. After filtration, a freshly prepared solution of diazomethane in diethyl ether was added, and the reaction mixture was stirred at room temperature for 30 min. The solvent was removed *in vacuo*, and the residue was chromatographed twice on silica (first run: petrol ether:ethyl acetate = 95:5; second run: CH_2Cl_2: petrol ether = 75:25) to yield 6.1 g (17.9 mmol, 88%) of **4**.

Method 2: A suspension of 500 mg of PtO_2 in 40 cm^3 of anhydrous acetic acid was hydrogenated for 30 min in a *Parr* apparatus at a pressure of 5 bar H_2. After addition of 2.5 g (7.18 mmol) of 5 (caution: Pt(0) is highly pyrophoric!), the mixture was hydrogenated for 18 h at a pressure of 5 bar, the colour of the solution changing from dark red to orange during this time. The catalyst was filtered off, and the acetic acid was removed *in vacuo*. The residue was dissolved in 50 cm^3 of CH_2Cl_2, and the solution was washed three times with saturated aqueous NH_4Cl solution and 100 cm^3 H_2O each. After drying over $MgSO_4$ and removal of the solvent, the residue was chromatographed on alumina (petrol ether: CH_2Cl_2 = 25:75) to yield 1.6 g (4.7 mmol, 66%) of **4**.

M.p.: 63–65°C; ^{1}H NMR: $\delta = 1.22$–1.45 (m, 3H), 1.52–1.86 (m, 6H), 2.32–2.44 (m, 2H), 2.55 (m, 1H), 3.68 (s, 3H), 4.00 (m, 1H), 4.03 (m, 3H), 4.07 (s, 5H) ppm; ^{13}C NMR: $\delta = 23.27$ (CH_2), 23.51 (CH_2), 26.36 (CH_2), 28.06 (CH_2), 31.68 (CH_2), 40.39, 44.45, 51.09, 67.11 (*Cp*), 67.20 (*Cp*), 68.51 (*Cp*), 68.61 (*Cp*), 69.06 (*Cp*), 87.28 (*Cp*), 175.20 (CO) ppm; MS: m/z (%) = 340 (100, M^+), 199 (91), 121 (48); $[\alpha]^{20}$ (nm) = 0.0 (589), 0.0 (587)° ($c = 1.26$, $CHCl_3$); CD (CH_2Cl_2, $1.05 \times 10^{-3}\,mol \cdot dm^{-3}$): λ_{max} ($\Delta\varepsilon$) = 333 (+0.015), 463 (−0.006), 567 (+0.004) nm.

2-Carbomethoxybenzoyl ferrocene (**5**; $C_9H_{16}FeO_3$)

To a solution of 12.0 g (64 mmol) of ferrocene in 120 cm^3 of *p.a.* CS_2 in a three-necked flask equipped with a condenser and a mechanical stirrer, a solution of 12.8 g (64 mmol) of 2-carbomethoxybenzoylchloride in 50 cm^3 dry diethyl ether was added quickly. After addition of a solution of 17.2 g (129 mmol) $AlCl_3$ in 50 cm^3 dry diethyl ether (caution: dissolving $AlCl_3$ in diethyl ether is a highly exothermic reaction!), the reaction mixture was refluxed for 2 h during which time the product separated as a highly viscous oil. After cooling the mixture to room temperature and separation of the solvent, the residue was hydrolyzed with 500 cm^3 of diluted HCl ($pH = 3$–4). The precipitated product was filtered off, washed with 250 cm^3 of H_2O, recrystallized from MeOH:H_2O = 1:1 (10 cm^3 of solvent per 1 g of product), and dried over $CaCl_2$ to give 15.1 g (43 mmol, 68%) of pure **5**.

M.p.: 139–141°C; ^{1}H NMR: $\delta = 3.62$ (s, 3H), 4.19 (s, 5H), 4.50 (s, 2H), 4.59 (s, 2H), 7.54 (m, 1H), 7.65 (m, 2H), 7.93 (m, 1H) ppm; ^{13}C NMR: $\delta = 52.14$ (CH_3), 69.81 (*Cp*), 70.00 (*Cp*), 72.40 (*Cp*), 79.83 (*Cp*), 127.62 (Ph), 129.22 (Ph), 129.55 (Ph), 129.75 (Ph), 131.99 (Ph), 142.11 (Ph), 166.88 (CO), 200.78 (CO) ppm; MS: m/z (%) = 348 (100, M^+), 283 (17), 253 (48), 235 (4), 225 (8), 197 (15), 161 (32), 121 (11), 89 (3), 81 (6), 69 (7), 56 (44).

(1S,2S)-2-Ferrocenylmethyl-cyclohexane-1-carboxylic acid (**6**; $C_{18}H_{22}FeO_2$)

A suspension of 5.75 g (16.9 mmol) of **4** in 100 cm^3 of 25% aqueous KOH solution was refluxed under Ar for 28 h. After filtration the solution was cooled with ice, and the product was precipitated with half-concentrated H_3PO_4. The yellow powder was filtered off, washed with H_2O, and dried over $CaCl_2$ to yield 3.9 g (12 mmol, 71%) of **6**.

M.p.: 51–54°C; ^{1}H NMR (*DMSO*-d_6): $\delta = 0.95$–1.17 (m, 3H), 1.21–1.60 (m, 6H), 2.10–2.26 (m, 3H), 3.75–4.00 (m, 9H) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 22.48$ (CH_2), 23.53 (CH_2), 23.53 (CH_2), 25.90 (CH_2), 27.38 (CH_2), 30.33 (CH_2), 39.55 (CH), 44.77 (CH), 66.71 (*Cp*), 66.99 (*Cp*), 68.05 (*Cp*),

68.25 (*Cp*), 68.48 (*Cp*), 87.52 (*Cp*), 176.03 (CO) ppm; MS: m/z (%) = 326 (67, M^+), 199 (100), 121 (99); $[\alpha]^{20}$ (nm) = 0.0 (589), 0.0 (578)° ($c = 0.86$, $CHCl_3$).

(4aS,8aS,R_m)-(4-Oxo-(η^5-5,6,7,8-tetrahydro-9H-benz[f]indenyl))-(η^5-cyclopentadienyl)-iron(II) (**7**; $C_{18}H_{20}FeO$) *and (4aR,8aS,S_m)-(4-oxo-(η^5-5,6,7,8-tetrahydro-9H-benz[f]indenyl))-(η^5-cyclopentadienyl)-iron(II)* (**16**; $C_{18}H_{20}FeO$)

A solution of 1.3 g (4 mmol) of **6** in 50 cm^3 CH_2Cl_2 was added dropwise to a solution of 1 g (4.8 mmol) trifluoracetic anhydride in 50 cm^3 CH_2Cl_2 at 0°C. The reaction mixture was stirred at this temperature for additional 5 h. To the dark red solution, 30 cm^3 of saturated aqueous $NaHCO_3$ solution were added, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 25 cm^3), and the combined organic layers were washed with H_2O (3 × 50 cm^3). After drying over $MgSO_4$ and removal of the solvent, the residue was chromatographed on silica (CH_2Cl_2:petrol ether = 95:5) to yield 0.8 g (2.6 mmol, 65%) of **7** and 75 mg (0.24 mmol, 6%) of **16**.

7: M.p.: 125–128°C; ^{1}H NMR: $\delta = 1.28$–1.74 (m, 8H), 2.40–2.75 (m, 4H), 4.14 (s, 5H), 4.44 (s, 1H), 4.45 (s, 1H), 4.81 (m, 1H) ppm; ^{13}C NMR: $\delta = 21.65$ (CH_2), 24.94 (CH_2), 25.31 (CH_2), 29.99 (CH_2), 35.18 (CH), 50.10 (CH), 65.31 (*Cp*), 70.00 (*Cp*), 70.24 (*Cp*), 70.78 (*Cp*), 74.04 (*Cp*), 91.53 (*Cp*), 207.91 (CO) ppm; MS: m/z (%): 308 (100, M^+), 199 (20), 121 (43); $[\alpha]^{20}$ (nm) = + 69.9 (598), + 73.8 (578)° ($c = 0.101$, $CHCl_3$); CD (CH_2Cl_2, 0.99×10^{-3} mol · dm^{-3}): λ_{max} ($\Delta\varepsilon$) = 240 (+ 1.70), 267 (+ 0.53), 302 (− 0.59), 340 (+ 0.68), 456 (+ 0.36), 531 (+ 0.05) nm.

16: M.p.: 122–123°C; ^{1}H NMR: $\delta = 1.05$–1.38 (m, 4H), 1.56–1.92 (m, 4H), 2.33–2.47 (m, 2H), 2.61–2.75 (m, 2H), 4.07 (s, 5H), 4.33 (m, 1H), 4.49 (m, 1H), 4.73 (m, 1H) ppm; ^{13}C NMR: $\delta = 25.58$ (CH_2), 25.82 (CH_2), 26.16 (CH_2), 32.55 (CH_2), 34.26 (CH_2), 41.35 (CH), 50.85 (CH), 64.51 (*Cp*), 70.02 (*Cp*), 70.27 (*Cp*), 70.90 (*Cp*), 74.73 (*Cp*), 91.69 (*Cp*), 205.51 (CO) ppm; MS: m/z (%) = 308 (100, M^+), 199 (19), 121 (41); $[\alpha]^{20}$ (nm) = + 85.4 (589), + 86.7 (578)° ($c = 0.315$, $CHCl_3$); CD (CH_2Cl_2, 0.98×10^{-3} mol · dm^{-3}): λ_{max} ($\Delta\varepsilon$) = 271 (+ 1.24), 304 (− 2.05), 336 (+ 1.79), 450 (+ 0.73), 521 (− 0.19) nm.

(4S,4aS,8aS,R_m)-(4-Hydroxy-(η^5-5,6,7,8-tetrahydro-4H,9H-benz[f]indenyl))-(η^5-cyclo-pentadienyl)-iron(II) (**8**; $C_{18}H_{22}FeO$)

To a suspension of 30 mg (0.8 mmol) of $LiAlH_4$ in 5 cm^3 of dry diethyl ether, a solution of 0.25 g (0.8 mmol) of **7** in 25 cm^3 of dry diethyl ether was added dropwise at − 12 to − 15°C. The colour changed from dark red to yellow. The reaction mixture was stirred for 1 h at − 15°C and then for one additional hour at room temperature. After addition of 5 cm^3 of H_2O the solution was filtered over celite. The organic layer was separated, washed with H_2O (2 × 25 cm^3), and dried over $MgSO_4$. After removal of the solvent the residue was chromatographed on silica (CH_2Cl_2) to yield 166 mg (0.54 mmol, 68%) of **8**.

M.p.: 149–151°C; ^{1}H NMR: $\delta = 0.78$–0.92 (m, 1H), 1.16–1.31 (m, 1H), 1.38 (OH, d, $J = 8.4$ Hz, 1H), 1.43–1.55 (m, 3H), 1.60–1.69 (m, 2H), 1.71–1.81 (m, 1H), 1.92–2.01 (m, 1H), 2.28 (H_B), 2.52 (H_A) (AB, $J_{AB} = 14.8$ Hz, $J_{AX} = 11.8$ Hz, $J_{BX} = 4.9$ Hz, 2H), 2.38–2.47 (m, 1H), 4.00 (s, 7H), 4.43 (s, 1H), 5.21 (t, $J = 6.9$ Hz, 1H) ppm; ^{13}C NMR: $\delta = 18.01$ (CH_2), 20.85 (CH_2), 23.86 (CH_2), 25.91 (CH_2), 30.93 (CH_2), 32.74 (CH), 42.90 (CH), 64.89 (*Cp*), 65.27 (*Cp*), 65.27 (*Cp*), 66.10 (*Cp*), 69.75 (*Cp*), 71.31 (CH), 84.06 (*Cp*), 86.18 (*Cp*) ppm; MS: m/z (%) = 310 (70, M^+), 121 (40), 49 (100); $[\alpha]^{20}$ (nm) = + 11.3 (589), + 11.5 (578)° ($c = 0.93$, $CHCl_3$); CD (CH_2Cl_2, 0.99×10^{-3} mol · dm^{-3}): λ_{max} ($\Delta\varepsilon$) = 269 (+ 0.12), 295 (− 0.10), 339 (+ 0.07), 445 (+ 0.05), 511 (− 0.01) nm.

(4S,4aS,8aS,R_m)-(4-N,N-Dimethylamino-(η^5-5,6,7,8-tetrahydro-4H,9H-benz[f]indenyl))-(η^5-cyclopentadienyl)-iron(II) (**9**; $C_{20}H_{27}FeN$)

A suspension of 70 mg (0.52 mmol) of $AlCl_3$ in 25 cm^3 1,2-dichloroethane was cooled to 0°C, and gaseous dimethylamine was added until complete consumption of $AlCl_3$ (an excess of dimethylamine

is recommended). A solution of 0.14 g (0.45 mmol) of **8** in 25 cm^3 1,2-dichloroethane was added slowly to this clear solution. The reaction mixture was stirred at 0°C for 30 min and then for additional 2 h at 50°C. After hydrolysis with 20 cm^3 of H_2O the organic layer was separated and the solvent was removed *in vacuo*. The residue was suspended with 25 cm^3 of 0.1 *N* KOH and extracted with diethyl ether (3×50 cm^3). The combined organic layers were washed with H_2O (3×50 cm^3) and dried over $MgSO_4$. The solvent was removed *in vacuo*, and the residue was chromatographed on silica (petrol ether:ethyl acetate:triethylamine = 79:20:1) to yield 85 mg (0.25 mmol, 56%) of **9**.

M.p.: 78–80°C; ^{1}H NMR: $\delta = 0.90$–1.07 (m, 1H), 1.14–1.30 (m, 1H), 1.34–1.53 (m, 3H), 1.57–1.76 (m, 3H), 2.05 (m, 1H), 2.28 (H_B), 2.50 (H_A) (AB, $J_{AB} = 13.0$ Hz, $J_{AX} = 12.3$ Hz, $J_{BX} = 4.9$ Hz, 2H), 2.44 (s, 6H), 3.98 (s, 6H), 4.01 (s, 1H), 4.24 (d, $J = 5.4$ Hz, 1H), 4.36 (s, 1H) ppm; ^{13}C NMR: $\delta =$ 20.61 (CH_2), 21.42 (CH_2), 24.36 (CH_2), 26.35 (CH_2), 31.40 (CH_2), 33.85 (CH), 42.27 (CH), 42.99 ($N(CH_3)_2$), 64.68 (*Cp*), 65.35 (*Cp*), 65.64 (CH), 66.62 (*Cp*), 69.87 (*Cp*), 83.85 (*Cp*), 85.05 (*Cp*) ppm; MS: m/z (%) = 337 (70, M^+), 291 (67), 121 (79), 56 (100); $[\alpha]^{20}$ (nm) = + 12.7 (589), + 13.0 (587)° ($c = 0.955$, $CHCl_3$).

(4aR,8aS,R_m)-(4-Oxo-(η^5-5,6,7,8-tetrahydro-9H-benz[f]indenyl))-(η^5-cyclopentadienyl)-iron(II) (**10**; $C_{18}H_{20}FeO$)

To a solution of 500 mg (1.6 mmol) of **7** in 10 cm^3 of *THF*, 1.25 cm^3 (2.5 mol) of a 2 *M LDA* solution in *THF* were added slowly at − 78°C, and the mixture was stirred at this temperature for 40 min. After quenching with 25 cm^3 of H_2O, the solution was allowed to warm to room temperature and extracted with CH_2Cl_2 (3×25 cm^3). The combined organic layers were washed with 3% HCl (3×30 cm^3), saturated $NaHCO_3$ solution (3×30 cm^3), and H_2O (3×30 cm^3) and dried over $MgSO_4$. After evaporation of the solvent the residue was chromatographed on silica (CH_2Cl_2:petrol ether:ethyl acetate = 4:1:5) to yield 418 mg (1.36 mmol, 83.6%) of **10**.

M.p.: 153–155°C; ^{1}H NMR: $\delta = 1.16$–1.40 (m, 4H), 1.65–1.71 (m, 1H), 1.76–1.82 (m, 1H), 1.85–1.95 (m, 1H), 2.09–2.20 (m, 2H), 2.45–2.52 (m, 1H), 2.54–2.63 (m, 1H), 4.15 (s, 5H), 4.39–4.40 (m, 1H), 4.40–4.43 (m, 1H), 4.81–4.82 (m, 1H) ppm; ^{13}C NMR: $\delta = 25.97$ (CH_2), 26.02 (CH_2), 26.16 (CH_2), 31.53 (CH_2), 34.28 (CH_2), 41.47 (CH), 52.46 (CH), 65.47 (*Cp*), 69.55 (*Cp*), 69.92 (*Cp*) 70.35 (*Cp*), 75.20 (*Cp*), 91.06 (*Cp*), 205.50 (CO) ppm; MS: m/z (%) = 308.2 (100, M^+), 198.9 (16.1), 120.8 (21.0), 55.8 (18.6); $[\alpha]^{20}$ (nm) = + 37.0 (589), + 38.3 (578)° ($c = 0.081$, $CHCl_3$); CD (CH_2Cl_2): $\lambda_{max}(\Delta\varepsilon) = 266$ (+ 0.47), 302 (− 0.70), 338 (+ 0.59), 455 (+ 0.30) nm.

(4S,4aR,8aS,R_m)-(4-Hydroxy-(η^5-5,6,7,8-tetrahydro-4H,9H-benz[f]indenyl))-(η^5-cyclo-pentadienyl)-iron(II) (**11a**; $C_{18}H_{22}FeO$) *and (4R,4aR,8aS,R_m)-(4-hydroxy-(η^5-5,6,7,8-tetrahydro-4H,9H-benz[f]indenyl))-(η^5-cyclopentadienyl)-iron(II)* (**11b**; $C_{18}H_{22}FeO$)

To a suspension of 170 mg (4.5 mmol) of $LiAlH_4$ in 15 cm^3 of diethyl ether, a solution of 900 mg (2.9 mmol) of **10** in 35 cm^3 of diethyl ether was added dropwise at 0°C. The reaction mixture was stirred at 0°C for 1 h and then for one additional hour at room temperature. H_2O (25 cm^3) was added, and the organic layer was separated. The aqueous layer was extracted with diethyl ether (2×20 cm^3), and the combined organic layers were washed with H_2O (3×25 cm^3) and dried over $MgSO_4$. After evaporation of the solvent the residue was chromatographed on silica (CH_2Cl_2), affording the two isomeric alcohols **11a** (505 mg, 1.63 mmol, 56.1%) and **11b** (255 mg, 0.82 mmol, 28.3%).

11a: M.p.: 151–153°C; ^{1}H NMR: $\delta = 0.99$–1.12 (m, 2H), 1.18–1.38 (m, 2H), 1.62–1.75 (m, 4H), 1.79–1.94 (m, 4H), 2.06 (OH, d, $J = 6.9$ Hz, 1H), 2.42–2.52 (m, 1H), 3.94 (dd, $J_1 = 4.2$ Hz, $J_2 = 6.7$ Hz, 1H) , 4.09–4.11 (m, 1H), 4.14–4.16 (m, 1H), 4.20 (s, 5H) ppm; ^{13}C NMR: $\delta = 26.09$ (CH_2), 26.51 (CH_2), 27.94 (CH_2), 32.61 (CH), 33.33 (CH_2), 34.24 (CH_2), 45.22 (CH), 64.50, 64.81, 65.50, 66.50 (*Cp*), 68.61, 87.01 (*Cp*), 94.69 (*Cp*) ppm; MS: m/z (%) = 310.3 (100, M^+), 292.2 (23.3), 291.2 (15.7), 225.1 (23.4), 223.0 (19.6), 221.0 (12.1), 172.1 (44.1), 129.0 (34.3), 128.8 (14.8), 120.9 (16.5),

114.9 (12.5); $[\alpha]^{20}$ (nm) = +9.4 (589), +9.6 (578)° ($c = 0.5$, $CHCl_3$); CD (CH_2Cl_2): λ_{max} ($\Delta\varepsilon$) = 246 (−0.21), 288 (−0.18), 475 (−0.06) nm.

11b: M.p.: 115–117°C; ^{1}H NMR: $\delta = 0.9$–1.0 (m, 1H), 1.04–1.17 (m, 2H), 1.19–1.48 (m, 2H), 1.39 (OH, d, $J = 2.5$ Hz, 1H), 1.73–1.99 (m, 5H), 2.25–2.33 (m, 1H), 2.49 (dd, $J_1 = 4.3$ Hz, $J_2 = 15.3$ Hz, 1H), 4.0–4.02 (m, 1H) 4.03 (s, 5H), 4.39–4.41 (m, 1H), 4.54–4.60 (m, 1H) ppm; ^{13}C NMR: $\delta = 26.04$ (CH_2), 26.09 (CH_2), 30.99 (CH_2), 32.60 (CH_2), 34.14 (CH_2), 37.73 (CH), 49.03 (CH), 64.80, 65.27, 66.26, 69.48 (*Cp*), 74.31, 85.04 (*Cp*), 86.91 (*Cp*) ppm; MS: m/z (%): 310.3 (100, M+), 292.2 (16.6), 291.2 (16.5), 238.1 (15.3), 222.0 (20.9), 129.0 (32.2), 128.0 (11.8), 120.9 (16.8); $[\alpha]^{20}$ (nm) = +22.1 (589), +23.9 (578)° ($c = 0.435$, $CHCl_3$); CD (CH_2Cl_2): λ_{max} ($\Delta\varepsilon$) = 264 (+0.12), 287 (−0.22), 444 (+0.04), 505 (−0.03) nm.

(4S,4aR,8aS,R_m)-(4-N,N-Dimethylamino-(η^5-5,6,7,8-tetrahydro-4H,9H-benz[f]indenyl))-(η^5-cyclopentadienyl)-iron(II) (**12**; $C_{20}H_{27}FeN$)

To a suspension of 165 mg (1.23 mmol) of $AlCl_3$ in 25 cm^3 1,2-dichloroethane, gaseous dimethylamine was added at 0°C until the solution becomes clear (an excess of dimethylamine is recommended). A solution of 320 mg (1.03 mmol) **11a** in 15 cm^3 1,2-dichloroethane was added dropwise to the $AlCl_3$–$NHMe_2$ solution within 30 min. The reaction mixture was stirred at 0°C for 1 h; then the temperature was increased to 40–45°C, and stirring was continued at this temperature for additional 16 h. The proceeding of the reaction was monitored *via* TLC (petrol ether:ethyl acetate:triethylamine = 79:20:1). When the reaction was completed, 50 cm^3 1% KOH were added, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 30 cm^3), and the combined organic layers were washed with H_2O (3 × 20 cm^3) and dried over $MgSO_4$. Chromatography on silica (petrol ether:ethyl acetate:triethylamine = 79:20:1) afforded 213 mg (0.63 mmol, 61.4%) of pure **12**.

M.p.: 92–94°C; ^{1}H NMR: $\delta = 0.93$–1.03 (m, 1H), 1.05–1.17 (m, 2H), 1.21–1.44 (m, 3H), 1.73–1.95 (m, 5H), 2.22 (s, 6H), 2.31 (dd, $J_1 = 3.2$ Hz, $J_2 = 16.02$ Hz, 1H), 3.55 (d, $J = 8.83$ Hz, 1H), 3.99 (t, $J = 2.2$ Hz, 1H), 4.0 (s, 5H), 4.03 (s, 1H), 4.25 (s, 1H) ppm; ^{13}C NMR: $\delta = 26.52$ (CH_2), 26.82 (CH_2), 32.36 (CH_2), 33.15 (CH_2), 34.59 (CH_2), 39.84 (CH), 41.67 (CH_3), 44.61 (CH), 64.65, 64.81, 65.35, 67.25, 69.37 (*Cp*), 87.53 (*Cp*), 91.81(*Cp*) ppm; MS m/z (%) = 338.3 (24.1), 337.3 (100, M^+), 294.1 (21.5), 293.2 (75.3), 292.2 (41.1), 291.2 (93.6), 255.0 (56.0), 253.0 (29.8), 225.0 (23.1), 221.0 (17.5), 164.9 (25.1); $[\alpha]^{20}$ (nm) = +56.6 (589), +61.3 (578)° ($c = 0.865$, $CHCl_3$); CD (CH_2Cl_2): $\lambda_{max}(\Delta\varepsilon)$ = 263 (+0.45), 293 (−0.12), 330 (+0.05), 456 (+0.18) nm.

Racemic trans-2-ferrocenoyl-cyclohexane-1-carboxylic acid (**13**; $C_{18}H_{20}FeO_3$)

A solution of 11.0 g (59.1 mmol) of ferrocene and of 5.0 g (32.5 mmol) of *trans*-cyclohexane-1,2-dicarboxylic acid anhydride in 100 cm^3 of CH_2Cl_2 was added dropwise to a suspension of 8.0 g (59.9 mmol) of $AlCl_3$ in 100 cm^3 of CH_2Cl_2. The mixture was stirred at room temperature for 2 h and subsequently poured on ice. The *pH* was adjusted to 2–3 with phosphoric acid (50%), and the organic layer was separated. The aqueous layer was extracted twice with 80 cm^3 CH_2Cl_2, and the combined organic layers were washed twice with 100 cm^3 of H_2O. After the organic phase was reduced to approximately 200 cm^3 *in vacuo* it was extracted with a 2 *N* aqueous NaOH solution (4 × 250 cm^3). Traces of organic solvents were removed from the aqueous layers *in vacuo*, and the product was precipitated by slow addition of H_3PO_4 (50%) at 5°C. The dark orange product was filtered off, washed with H_2O, and dried over $CaCl_2$ to yield 7.3 g (22.8 mmol, 68%) of **13**.

M.p.: decomposition above 175°C; ^{1}H NMR: $\delta = 1.10$–1.60 (m, 4H), 1.70–1.90 (m, 2H), 2.20–2.20 (m, 2H), 2.70–2.90 (m, 1H), 2.90–3.10 (m, 1H), 4.20 (s, 5H), 4.50 (s, 1H), 4.70 (s, 1H), 4.90 (s, 1H) ppm; ^{13}C NMR: $\delta = 25.40$ (CH_2), 25.80 (CH_2), 29.30 (CH_2), 31.00 (CH_2), 43.80, 67.90, 70.0 (*Cp*), 71.80, 71.90, 77.80 (*Cp*), 180.90 (CO), 207.00 (CO) ppm; MS: m/z (%): 340.1 (100, M^+), 294.1 (10.4), 213.0 (56.2), 199.1 (12.6), 186.0 (49.3), 165.1 (10.3), 129.0 (39.4), 121.0 (59.0), 109.0 (20.7), 94.9 (22.4), 81.0 (18.8), 55.9 (39.3), 48.9 (10.0), 41.0 (15.0).

Racemic trans-2-ferrocenylmethyl-cyclohexane-1-carboxylic acid monomethylester (**14**; $C_{19}H_{24}FeO_2$)

To a solution of 3.4 g (10.6 mmol) of **13** in 110 cm^3 of MeOH, 17 cm^3 of benzene, 17 cm^3 of H_2O, and 17 cm^3 of concentrated HCl, freshly prepared zinc amalgam was added, and the mixture was refluxed for 15 h. After cooling to room temperature the amalgam was filtered off and washed with benzene. The organic layer was washed with brine ($2 \times 100\,cm^3$) and H_2O ($2 \times 50\,cm^3$) and dried over $MgSO_4$. After filtration, a freshly prepared solution of diazomethane in diethyl ether was added, and the reaction mixture was stirred at room temperature for 1 h. The solvent was removed *in vacuo*, and the residue was chromatographed twice on silica (first run: petrol ether:ethyl acetate = 95:5; second run: CH_2Cl_2:petrol ether = 75:25) to yield 2.09 g (6.14 mmol, 58%) of **14**.

M.p.: 37–39°C; ^{1}H NMR: $\delta = 0.80$–0.90 (m, 1H), 1.10–1.20 (m, 2H), 1.30–1.40 (m, 1H), 1.50–1.70 (m, 4H), 1.80–1.90 (m, 1H), 2.00–2.10 (m, 1H), 2.10 (dd, $J_1 = 8.1$ Hz, $J_2 = 14.1$ Hz, 1H), 2.40 (dd, $J_1 = 3.9$ Hz, $J_2 = 13.8$ Hz, 1H), 3.70 (s, 3H), 4.00 (s, 4H), 4.10 (s, 5H) ppm; ^{13}C NMR: $\delta = 25.30$ (CH_2), 25.50 (CH_2), 30.20 (CH_2), 30.70 (CH_2), 35.40 (CH_2), 40.60, 49.20, 51.40, 67.10 (*Cp*), 67.30 (*Cp*), 68.50 (*Cp*), 69.10 (*Cp*), 85.80 (*Cp*), 176.60 (CO) ppm; MS: m/z (%) = 340.2 (100, M^+), 212.8 (16.5), 198.9 (70.0), 168.0 (10.6), 154.9 (14.0), 139.9 (41.1), 125.8 (30.1), 120.7 (57.5), 107.8 (45.0), 80.8 (81.8), 66.9 (25.2), 55.8 (20.6), 54.8 (16.1), 40.8 (20.4), 38.8 (12.7).

Racemic trans-2-ferrocenylmethyl-cyclohexane-1-carboxylic acid (**15**; $C_{18}H_{22}FeO_2$)

A suspension of 1.0 g (2.94 mmol) of **14** in 50 cm^3 of aqueous KOH (20%) was refluxed under Ar for 25 h. After filtration, the solution was cooled with ice, and the product was precipitated with H_3PO_4 (50%). The yellow powder was washed with H_2O and dried over $CaCl_2$ to yield 0.680 g (2.08 mmol, 70.7%) of crude **15** which was used in the subsequent reaction without further purification.

(4aS,8aR*,R^*_m)-(4-Oxo-(η^5-5,6,7,8-tetrahydro-9H-benz[f]indenyl))-(η^5-cyclopenta-dienyl)-ion(II)* (**16**; $C_{18}H_{20}FeO$) *and (4aR*,8aR*,S^*_m)-(4-oxo-(η^5-5,6,7,8-tetrahydro-9H-benz[f]indenyl))-(η^5-cyclopentadienyl)-ion(II)* (**7**; $C_{18}H_{20}FeO$)

To a solution of 1 cm^3 (7.2 mmol) of trifluoroacetic acid anhydride in 60 cm^3 CH_2Cl_2, 7 g of molecular sieve (4 Å) and (dropwise) a suspension of 650 mg (1.99 mmol) of **14** in 60 cm^3 CH_2Cl_2 were added at -15 to -5°C. After stirring at room temperature for 4 h the reaction mixture was filtered over celite. The mixture was hydrolyzed with saturated aqueous $NaHCO_3$ solution, and the organic layer was separated. The aqueous layer was extracted twice with 50 cm^3 of CH_2Cl_2, and the combined organic layers were washed four times with 70 cm^3 of H_2O. After drying over $MgSO_4$ and removal of the solvent *in vacuo*, the residue was chromatographed on silica (CH_2Cl_2:petrol ether = 95:5) to afford 481 mg (1.56 mmol, 78%) of **16** and 25 mg (0.08 mmol, 4%) of **7**. For physical and spectroscopic data of **7** and **16**, see above.

(4R,4aS*,8aR*,R^*_m)-(4-Hydroxy-(η^5-5,6,7,8-tetrahydro-4H,9H-benz[f]-indenyl))-(η^5-cyclopentadienyl)-iron(II)* (**17**; $C_{18}H_{22}FeO$)

To a suspension of 35 mg (0.9 mmol) of $LiAlH_4$ in 5 cm^3 dry diethyl ether, a solution of 0.19 g (0.6 mmol) of **16** in 15 cm^3 dry diethyl ether was added dropwise at -10 to -15°C. The mixture was stirred at this temperature for an additional hour and then for 1 h at room temperature. The excess of hydride was destroyed by slow addition of 5 cm^3 of H_2O, and the reaction mixture was filtered over celite. The organic layer was separated and washed twice with 25 cm^3 of H_2O. After drying over $MgSO_4$ and removal of the solvent *in vacuo*, the residue was chromatographed on silica (CH_2Cl_2) to afford 147 mg (0.47 mmol, 78%) of **17**.

M.p.: 142–144°C; ^{1}H NMR: $\delta = 0.93$–1.13 (m, 2H), 1.14–1.34 (m, 3H), 1.40–1.51 (m, 1H), 1.64–1.85 (m, 3H), 1.76 (d, $J = 9.3$ Hz, OH), 2.25–2.39 (m, 2H), 2.39–2.46 (m, 1H), 3.76 (t, $J = 9.3$ Hz, 1H), 3.99 (m, 1H), 4.05 (m, 1H), 4.11 (s, 5H), 4.18 (m, 1H) ppm; ^{13}C NMR: $\delta = 25.93$ (CH_2), 25.99 (CH_2), 30.09 (CH_2), 31.99 (CH_2), 34.04 (CH_2), 37.78 (CH), 48.27 (CH), 61.96 (*Cp*), 65.94 (*Cp*), 66.26 (*Cp*), 69.12 (*Cp*), 71.55 (CH), 86.37 (*Cp*), 91.45 (*Cp*) ppm; MS: m/z (%) = 310 (100, M^+), 292 (39), 263 (3), 225 (24), 199 (7), 172 (39), 165 (16), 129 (46), 121 (14), 91 (15), 81 (6), 56 (9), 43 (2).

(1S,2R)-Cyclohexane-1,2-dicarboxylic acid monomethylester (**19**; $C_9H_{14}FeO_4$)

A suspension of 1 g of PtO_2 in 50 cm^3 MeOH was hydrogenated for 40 min in a *Parr* apparatus at a pressure of 4 bar H_2. After addition of 4.8 g (26 mmol) of (1*S*,2*R*)-cyclohex-4-ene-1,2-dicarboxylic acid monomethylester (caution: Pt(0) is highly pyrophoric!), the mixture was hydrogenated for 18 h at a pressure of 5 bar. The catalyst was filtered off, and MeOH was removed *in vacuo* to afford a yellow oil which was dried *in vacuo* to yield 4.4 g (24 mmol, 92%) of **19**.

M.p.: 63–65°C; ^{1}H NMR: $\delta = 1.32$–1.61 (m, 4H), 1.68–1.83 (m, 2H), 1.93–2.07 (m, 2H), 2.76–2.88 (m, 2H), 3.66 (s, 3H) ppm; ^{13}C NMR: $\delta = 23.59$ (CH_2), 23.72 (CH_2), 25.91 (CH_2), 26.23 (CH_2), 42.31 (CH), 42.51 (CH), 51.66 (CH_3), 174.02 (CO), 180.13 (CO) ppm; MS: m/z (%) = 186 (2, M^+), 168 (54), 155 (71), 140 (84), 126 (85), 99 (16), 95 (10), 87 (32), 81 (100), 67 (75), 45 (13); $[\alpha]^{20}$ (nm) = +4.9 (589), +5.2 (578), +21.5 (365)° ($c = 2.37$, EtOH).

(1S,2R)-2-Ferrocenoyl-cyclohexane-1-carboxylic acid monomethylester (**20**; $C_{19}H_{22}FeO_3$)

To a solution of 3.5 g (19 mmol) of **19** in 25 cm^3 of dry benzene, 1.7 cm^3 (21 mmol) of pyridine and 4.2 cm^3 (56 mmol) of $SOCl_2$ were added. After stirring the solution for 2 h at room temperature and for additional 18 h at 40°C the solvent was removed *in vacuo*. In order to get rid of $SOCl_2$, the residue was dissolved twice in 50 cm^3 benzene which was subsequently removed under reduced pressure. A mixture of an oil and of colourless crystals (pyridinium hydrochloride) was obtained. The product was dissolved in 40 cm^3 of diethyl ether and stored at 0°C.

The solution of the acid chloride was filtered under exclusion of H_2O over celite into a three necked flask; then, a solution of 3.5 g (19 mmol) of ferrocene in 40 cm^3 of CS_2 was added. After addition of a solution of 5 g (38 mmol) of $AlCl_3$ in 30 cm^3 of dry diethyl ether (caution: dissolving $AlCl_3$ in diethyl ether is a highly exothermic reaction!) the reaction mixture was refluxed for 4 h, and the product was separated as a highly viscous oil. After cooling the mixture to room temperature and separation of the solvent, the residue was hydrolyzed with 150 cm^3 of diluted HCl ($pH = 3$–4). The product precipitates as an orange oil. The aqueous layer was extracted twice with 100 cm^3 of H_2O, and the combined organic layers were washed three times with 100 cm^3 of H_2O. After drying over $MgSO_4$ and evaporation of the solvent the residue was chromatographed on silica (petrol ether:ethyl acetate = 9:1) to afford 2.2 g (6.2 mmol, 33%) of an orange oil.

^{1}H NMR: $\delta = 1.23$–1.49 (m, 3H), 1.72–1.83 (m, 2H), 1.86–1.95 (m, 1H), 2.08–2.20 (m, 1H), 2.23–2.32 (m, 1H), 2.58 (m, 1H), 3.47 (m, 1H), 3.67 (s, 3H), 4.24 (s, 5H), 4.45 (m, 1H), 4.48 (m, 1H), 4.69 (m, 1H), 4.83 (m, 1H) ppm; ^{13}C NMR: $\delta = 22.91$ (CH_2), 24.31 (CH_2), 25.46 (CH_2), 28.95 (CH_2), 42.75 (CH), 46.57 (CH), 51.54 (CH_3), 69.02 (*Cp*), 69.83 (*Cp*), 70.10 (*Cp*), 71.64 (*Cp*), 71.75 (*Cp*), 78.16 (*Cp*), 174.76 (CO), 206.00 (CO) ppm; MS: m/z (%) = 354 (100, M^+), 323 (21), 289 (5), 257 (16), 213 (82), 185 (76), 149 (20), 129 (66), 121 (66), 92 (19), 81 (18), 56 (27), 43 (13); $[\alpha]^{20°}$ (nm) = +27.6 (589), +27.8 (578)° ($c = 1.375$, $CHCl_3$).

Grignard cross coupling reactions (general procedure)

A solution of 0.03 mmol of the catalyst precursor (**1** · $PdCl_2$ or **2** · $PdCl_2$) in diethyl ether was degassed, and 0.7 cm^3 (10 mmol) of vinylbromide and 21 mmol of a solution of phenylethylmagnesium chloride in diethyl ether were added at −78°C. After stirring for 24 h at 0°C, 1.5 g of dry ice were added, and

the reaction mixture was stirred for additional 15 min. The solution was extracted with H_2O, and the organic layer was separated. The aqueous layer was extracted with diethyl ether, and the combined organic layers were washed once with saturated $NaHCO_3$ solution and twice with H_2O. After drying over $MgSO_4$ the solvent was evaporated, and the residue was purified by bulb-to-bulb distillation (100°C, 14 torr). The chemical purity was determined by ^1H NMR spectroscopy, the enantiomeric purity by GC on FS-Lipodex C, 50 m × 0.25 mm (carrier: H_2, column temperature: 29°C, split: 1:100, injector temperature: 175°C, sample: 30 mg/cm^3 in CH_2Cl_2, injected 0.5 mm^3).

X-Ray analyses

Crystallographic data were collected on a modified STOE diffractometer using graphite monochromated MoK_α radiation ($\lambda = 0.71069$ Å). Data collections performed at low temperatures involved the use of a home-built coldstream low-temperature device. Structures were solved with direct methods and refined with least-squares, including anisotropic atomic displacement parameters for all non-hydrogen atoms. No absorption or extinction corrections were applied, and H atoms were included at calculated positions. Data pertaining to the crystallographic characterization, data collection, and structure refinement are summarized in Table 1, computer programs used for structure solution and refinement are listed in Ref [9]. Atomic coordinates have been deposited at the Cambridge Crystallographic Data Centre (deposition numbers CCDC 180283–180289).

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