ELSEVIER

Journal of Organometallic Chemistry 508 (1996) 195–208

Journal of Organo metallic Chemistry

Isomeric diphosphines of a heteroannularly bridged ferrocene: preparation, chromatographic separation and structure elucidation

Georg Kutschera [a], Christoph Kratky [b], Walter Weissensteiner [a], Michael Widhalm [a,*]

[a] *Institut für Organische Chemie, Universität Wien, Währingerstraße 38, A-1090 Wien, Austria*
[b] *Institut für Physikalische Chemie, Universität Graz, Heinrichstraße 28, A-8010 Graz, Austria*

Received 20 June 1995

Abstract

Twofold lithiation of the heteroannularly bridged aminophosphine **5** yielded a mixture of five isomeric aminodiphosphines **7a–7d** and **11**, which were separated by adsorption chromatography. Their substitution pattern was elucidated by X-ray structure analyses and chemical correlation. Corresponding diphosphines **10a–10d** were derived with moderate yields via acetates **8a–8d**. A search for stable conformers of **7a–7d** and **11** was conducted using empirical force field calculations. Calculated minimum-energy geometries were compared with crystal structures of **7a**, **7c** and **7d**.

Keywords: Iron; Heteroannularly-bridged ferrocene; Diphosphine; X-ray structure; Circular dichroism

1. Introduction

Following the successful use of ferrocene derivatives as catalysts in asymmetric cross-coupling reactions, attention has focused on structural variations of 1-diphenylphosphino-2-(1-*N*,*N*-dimethylaminoethyl)-ferrocene (**2**), which was originally employed by Kumada's group [1]. Subsequently a second phosphino group was introduced at the unsubstituted cyclopentadiene ring to yield **3** with an additional site for transition metal coordination. Moreover, the ethylamino group was transformed into ethyl, methoxyethyl on acetoxyethyl, or into more complex "side arms" with additional heteroatoms to support a stereoselective coordination of the substrate at the transition metal. So far more than 200 ferrocenyl-based ligands have been designed in the quest for chiral catalysts for a variety of asymmetric reactions, including hydrogenation, hydrosilylation, cross-coupling reactions and aldol condensation [2]. Most of these catalysts were synthesized from *N*,*N*-dimethyl-1-ferrocenylethylamine (**1**) as a key intermediate [3], which permitted a highly diastereoselective access to planar-chiral derivatives via ortho-lithiation. An additional advantage is the availability of a convenient procedure for optical resolution of **1** via diastereomeric tartrates, permitting the facile preparation of optically active derivatives [4].

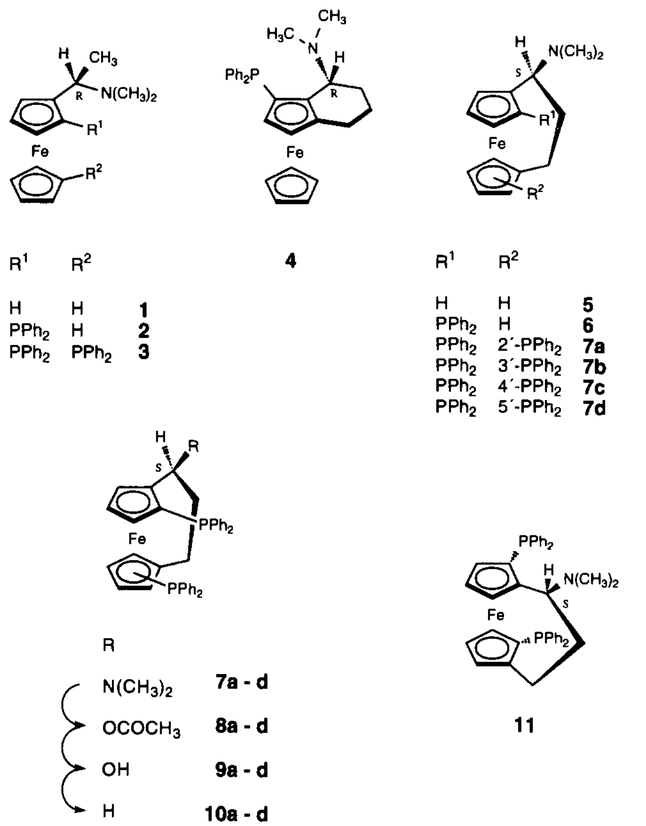
As it is generally accepted that the catalyst's conformational stability favours high diastereoselectivity [5], we set out to synthesize homoannularly and heteroannularly bridged ferrocenes with phosphorus and nitrogen as coordination sites. Thus we recently prepared the homoannularly bridged compound **4** and tested its efficiency in asymmetric cross-coupling reactions [6]. In the preceding paper, we described the synthesis of aminomonophosphine **6**, derived from the heteroannularly bridged ferrocene **5** [7]. Here we report the synthesis and chromatographic separation of five isomeric aminodiphosphines **7a–7d** and **11** obtained by twofold lithiation of **5**, and the elucidation of their substitution pattern and molecular conformation by both chemical and physical methods.

2. Results and discussion

Ortho-lithiation of **5** with *n*-BuLi exhibited high diastereoselectivity, similar as observed for the non-bridged aminoferrocene **1**. In each case, quenching the reaction with electrophiles such as benzophenone [8] or chlorodiphenylphosphine [7] led to the predominant formation of a single diastereomer. Excess of *n*-BuLi–

* Corresponding author.

SSDI 0022-328X(95)05849-4



Scheme 1.

TMEDA introduced a second Li atom at the opposite cyclopentadiene ring, resulting in up to four isomers, as a consequence of the non-equivalence of positions 2′–5′ (Scheme 1). Thin layer chromatography (TLC) analysis of the reaction mixture shows several well-separated spots, indicating that all four possible diastereomers are indeed produced and should be separable by chromatographic methods. Since the reaction products were observed to be stable towards oxidation, a conventional column chromatography on silica gel under gravity with ethylacetate–petroleum ether–triethylamine as eluent could be employed for preparative scale separation to yield the five diphosphine products in significant amounts. One diphosphine predominated and was isolated with 44% yield, well separated from four isomeric diphosphines which were obtained with low yields (2–7%). In addition some monophosphine **6** was also recovered from the reaction mixture to give a total yield of approximately 100%. Four of the isomers could be obtained as orange to brown crystals. All of them were characterized by spectroscopic methods (^{1}H, ^{13}C, ^{31}P NMR and mass spectroscopy (MS)).

In the preceding communication we demonstrated that the first lithiation step selectively forms the 2-lithio derivative [7], and there is undoubtful NMR evidence from homonuclear and heteronuclear shift correlation experiments that the second lithium atom is introduced into the opposite ring [9]. Thus four structures, **7a–7d**, had to be assigned to four of the five isomers obtained.

Contrary to benzoid compounds, the substitution pattern in ferrocenes cannot be deduced from the magnitude of the coupling constants J_{HH} of ring protons since J_{HH} is only 1–3 Hz and multiplets are not well resolved. We therefore carried out crystal structure analyses on those compounds that yielded suitable crystals. This permitted unambiguous assignment of configurations **7a**, **7c** and **7d** (see Figs. 3–5 later) to the diphosphines isolated from fractions 2, 3 and 1 respectively.

The decision as to which of the remaining two compounds (fractions 4 and 5) would be the isomer **7b** was based on a combination of chemical correlation and spectroscopy. Transformation of amines **7a–7d** into the corresponding hydrocarbons **10a–10d** was performed by a two- or three-step sequence (see Scheme 1). The diphosphine of fraction 4 yielded a C_1-symmetrical hydrocarbon, which is in agreement with structure **7b**, while deamination of **7a** (fraction 2) and diphosphine of fraction 5 afforded identical products (**10a**) as judged from ^{13}C NMR spectroscopy. Consequently the aminodiphosphine of fraction 5 was identified as **11** obviously formed from the small amount of **5** lithiated at C(5). Characteristic properties relevant for the structural assignments are listed in Table 1.

Since the optically active ligands [10] are of interest in view of their projected application in asymmetric catalysis, we prepared (*S*)-**7a–7d** and **11** from (−)(*S*)-**5** and recorded their CD spectra (Fig. 1). The short-wavelength range (250–400 nm) was found to be largely congruent, but distinct differences were observed in the range of the "ferrocene band" between 400 and 600 nm. Compound, **7b–7d** show positive Cotton effects of similar strength ($\Delta\varepsilon = 2.1$–3.1); these were found to be diminished for **7a** and **11**. Moreover, for **7a** the sign was inverted [11]. ^{31}P NMR spectra were recorded of all

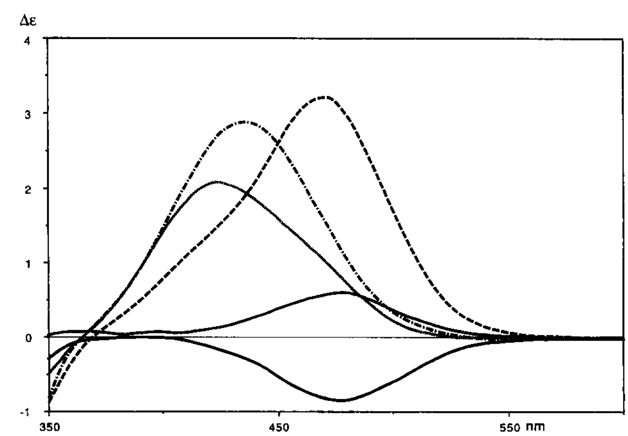
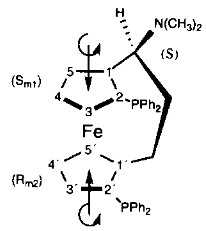


Fig. 1. CD spectra of **7a** (———), **7b** (-----), **7c** (–·–·–·–·), **7d** (······), and **11** (———), derived from (*S*)-**5**.

Table 1
Characteristic properties relevant for the structural assignments

Compound	Chromatographic fraction	δ (^{31}P) (ppm)	J_{PP} (Hz)	CD, λ_{max} ($\Delta\varepsilon$) (nm)					δ (^{31}P) (ppm)	Symmetry
7a	2	−24.30 (d), −24.77 (d)	43.9	260 (−27.6)			474 (−0.848)	→ **10a**	−25.92 (s)	C_s
7b	4	−20.10 (s), −21.70 (s)	0.0	243 (−2.24)	274 (+11.42)	340 (−1.21)	470 (+3.22)	→ **10b**	−18.85 (s), −20.60 (s)	C_1
7c	3	−16.68 (s), −21.61 (s)	0.0	251 (−12.5)		332 (−2.30)	436 (+2.98)	→ **10c**	−15.84 (s), −21.19 (s)	C_1
7d	1	−22.09 (s), −21.79 (s)	0.0	257 (−18.1)			424 (+2.07)	→ **10d**	−21.11 (s)	C_2
11	5	−25.01 (d), −26.48 (d)	48.4	256 (+8.10)	283 sh (+2.76)		475 (+0.572)	→ **10a**	−25.92 (s)	C_s



(S)(S_{m1})(R_{m2})-**7a**

isomers and showed a marked dependence of shift values from the substitution pattern. For **7a** and **11** with direct opposition of diphenylphosphino groups an up-field shift of up to 9 ppm relative to **7b**–**7d** is observed. Similar P–P coupling constants were found for **7a** and **11**, but virtually no P–P coupling occurred in **7b**–**7d**. We attribute this behavior to the nearly eclipsed conformation of cyclopentadienyl (Cp) rings in **7** (see below) which results in a perfect arrangement of phosphorus atoms for interaction either through space or with involvement of the iron atom.

To expand the scope of this new class of ferrocenyldiphosphines we also prepared acetates and hydrocarbons of **7**. Acetates **8** were accessible with a good to excellent yield by refluxing the amines **7** with acetic anhydride. The hydrocarbons **10** were finally obtained with a moderate yield by reduction with $AlCl_3$–$LiAlH_4$.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms in the crystal structure of **7a**, where U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor and the atomic numbering is defined in Fig. 2

	x/a ($\times 10^{-4}$)	y/b ($\times 10^{-4}$)	z/c ($\times 10^{-4}$)	U_{eq} ($\times 10^{-3}$ Å^2)
Fe(1)	8622(1)	435(1)	1797(1)	17(1)
P(1)	6924(1)	−221(1)	164(1)	18(1)
P(2)	7769(1)	2511(1)	226(1)	17(1)
N(1)	8068(2)	−1108(3)	−1211(3)	20(1)
C(1)	8481(2)	−616(3)	663(4)	18(1)
C(2)	7807(2)	−480(3)	1045(3)	18(1)
C(3)	7968(2)	−652(3)	2193(4)	20(1)
C(4)	8711(2)	−909(3)	2526(4)	19(1)
C(5)	9027(2)	−903(3)	1584(4)	20(1)
C(11)	9056(2)	1431(3)	965(4)	18(1)
C(12)	8414(2)	1843(3)	1255(4)	17(1)
C(13)	8516(2)	1810(3)	2429(4)	18(1)
C(14)	9215(2)	1412(3)	2851(4)	21(1)
C(15)	9553(2)	1207(3)	1960(4)	22(1)
C(21)	8606(2)	−495(3)	−483(3)	19(1)
C(22)	8577(2)	565(3)	−873(4)	20(1)
C(23)	9157(2)	1224(3)	−181(4)	20(1)
C(31)	8186(3)	−2119(3)	−894(4)	24(1)
C(32)	8089(3)	−1017(4)	−2371(4)	29(1)
C(41)	6359(2)	19(3)	1182(4)	20(1)
C(42)	6578(3)	693(3)	2020(4)	23(1)
C(43)	6115(3)	958(4)	2707(4)	26(1)
C(44)	5423(3)	576(4)	2548(4)	27(1)
C(45)	5192(3)	−86(4)	1710(4)	28(1)
C(46)	5658(2)	−368(4)	1033(4)	22(1)
C(51)	6632(2)	−1468(3)	−244(4)	21(1)
C(52)	6352(2)	−1655(4)	−1349(4)	26(1)
C(53)	6155(3)	−2599(4)	−1690(5)	35(1)
C(54)	6234(3)	−3352(4)	−951(5)	38(1)
C(55)	6496(3)	−3169(4)	144(5)	35(1)
C(56)	6700(3)	−2235(3)	505(4)	26(1)
C(61)	8241(2)	3698(3)	386(4)	18(1)
C(62)	8980(2)	3805(3)	853(4)	22(1)
C(63)	9311(3)	4710(3)	877(4)	23(1)
C(64)	8914(3)	5520(3)	465(4)	24(1)
C(65)	8179(3)	5431(3)	15(4)	23(1)
C(66)	7849(3)	4526(3)	−33(4)	22(1)
C(71)	6991(2)	2799(3)	844(4)	20(1)
C(72)	6305(2)	2510(3)	284(4)	21(1)
C(73)	5688(3)	2764(4)	668(4)	28(1)
C(74)	5750(3)	3303(4)	1611(4)	30(1)
C(75)	6431(3)	3590(3)	2182(4)	25(1)
C(76)	7049(2)	3336(3)	1812(4)	21(1)

A one-step conversion of **8** to **10** succeeded in one case (**10b**), while **10a**, **10c** and **10d** were only accessible after isolation of the intermediate alcohols **9a**, **9c** and **9d** and subsequent treatment with $AlCl_3$–$LiAlH_4$. As expected, NMR spectroscopy revealed C_1 symmetry (**10b** and **10c**) for two of them, but C_s or C_2 symmetry for **10a** and **10d** respectively.

2.1. Force field calculations and crystal structure determinations

In order to get insight into stability and minimum-energy conformations of aminodiphosphines, force field calculations were conducted for all aminophosphines using the program PCMODEL [12] and minimum geometries were compared with X-ray structural analyses of **7a**, **7c** and **7d** (Tables 2–5). All crystal structures show similar general shape with same conformation of the C_3 bridge (Figs. 2–5). Minor differences arising from different substitution pattern are listed in Table 6. Since the torsional angle of Cp rings is determined by the conformation of the C_3 bridge which is stabilized in the *out-of-plane* conformation (Fig. 6A) obviously caused by steric interaction with the PPh_2 group adjacent at Cp(1) in all cases similar torsional angles (5.3–6.2°) are found. The same is true for the tilt angle of the Cp

Table 3
Coordinates and displacement parameters for the crystal structure of **7c**

	x/a ($\times 10^{-4}$)	y/b ($\times 10^{-4}$)	z/c ($\times 10^{-4}$)	U_{eq} ($\times 10^{-3}$ Å^2)
Fe(1)	2763(1)	4265(1)	7621(1)	18(1)
P(1)	4266(1)	1864(1)	6600(1)	19(1)
P(2)	−27(1)	6821(1)	7618(1)	21(1)
N(1)	6740(2)	1675(2)	7930(1)	26(1)
C(1)	4819(3)	3518(2)	7586(2)	21(1)
C(2)	4312(2)	3390(2)	6834(2)	19(1)
C(3)	3741(2)	4686(2)	6355(2)	20(1)
C(4)	3898(3)	5596(3)	6783(2)	23(1)
C(5)	4583(3)	4884(2)	7526(2)	22(1)
C(11)	2129(3)	3201(3)	8826(2)	24(1)
C(12)	1516(3)	2920(3)	8190(2)	24(1)
C(13)	732(3)	4103(2)	7718(2)	23(1)
C(14)	810(3)	5144(2)	8071(2)	21(1)
C(15)	1662(3)	4569(3)	8764(2)	23(1)
C(21)	5459(3)	2439(2)	8315(2)	23(1)
C(22)	4446(3)	1545(3)	8885(2)	26(1)
C(23)	3165(3)	2252(3)	9387(2)	26(1)
C(31)	7714(3)	2541(3)	7437(2)	35(1)
C(32)	7460(3)	629(3)	8588(2)	37(1)
C(41)	5923(3)	1551(2)	5896(2)	21(1)
C(42)	6726(3)	2493(3)	5450(2)	23(1)
C(43)	7917(3)	2187(3)	4880(2)	27(1)
C(44)	8322(3)	941(3)	4759(2)	31(1)
C(45)	7544(3)	−4(3)	5208(2)	36(1)
C(46)	6339(3)	299(3)	5770(2)	29(1)
C(51)	3068(3)	2532(2)	5767(2)	21(1)
C(52)	3481(3)	3079(3)	4878(2)	29(1)
C(53)	2512(3)	3626(3)	4289(2)	32(1)
C(54)	1101(3)	3635(3)	4584(2)	29(1)
C(55)	674(3)	3086(3)	5459(2)	28(1)
C(56)	1647(3)	2527(3)	6044(2)	24(1)
C(61)	594(3)	7689(2)	8242(2)	22(1)
C(62)	1471(3)	8557(2)	7783(2)	23(1)
C(63)	1974(3)	9252(3)	8215(2)	27(1)
C(64)	1582(3)	9092(3)	9109(2)	30(1)
C(65)	702(3)	8232(3)	9573(2)	28(1)
C(66)	211(3)	7527(3)	9142(2)	24(1)
C(71)	−1830(3)	6801(3)	8159(2)	23(1)
C(72)	−2272(3)	5721(3)	8771(2)	27(1)
C(73)	−3674(3)	5773(3)	9107(2)	32(1)
C(74)	−4651(3)	6902(3)	8845(2)	35(1)
C(75)	−4228(3)	7973(3)	8239(2)	39(1)
C(76)	−2829(3)	7927(3)	7890(2)	33(1)

Table 4
Coordinates and displacement parameters for the crystal structure of **7d**

	x/a ($\times 10^{-4}$)	y/b ($\times 10^{-4}$)	z/c ($\times 10^{-4}$)	U_{eq} ($\times 10^{-3}$ Å^2)
Fe(1)	3571(1)	7265(1)	1296(1)	19(1)
P(1)	5118(1)	6305(1)	3606(1)	21(1)
P(2)	211(1)	8367(1)	−125(1)	22(1)
N(1)	2243(3)	8417(2)	3863(2)	25(1)
C(1)	3162(3)	8145(2)	2280(2)	20(1)
C(2)	4688(3)	7384(2)	2473(2)	20(1)
C(3)	5626(3)	7617(2)	1602(2)	22(1)
C(4)	4725(3)	8501(2)	890(2)	23(1)
C(5)	3233(3)	8829(2)	1314(2)	23(1)
C(11)	1612(3)	6701(2)	1567(2)	22(1)
C(12)	2969(3)	5826(2)	1787(2)	24(1)
C(13)	3912(3)	5838(2)	920(2)	24(1)
C(14)	3130(3)	6691(2)	149(2)	23(1)
C(15)	1698(3)	7229(2)	534(2)	22(1)
C(21)	1748(3)	8234(2)	2958(2)	23(1)
C(22)	1019(3)	7245(2)	3186(2)	26(1)
C(23)	380(3)	7061(2)	2280(2)	24(1)
C(31)	2869(3)	9383(2)	3646(2)	30(1)
C(32)	960(4)	8543(3)	4573(2)	39(1)
C(41)	5718(3)	6961(2)	4456(2)	22(1)
C(42)	6637(3)	7706(2)	4192(2)	26(1)
C(43)	7020(3)	8179(2)	4881(2)	31(1)
C(44)	6530(3)	7885(2)	5841(2)	35(1)
C(45)	5649(4)	7131(2)	6118(2)	35(1)
C(46)	5224(3)	6681(2)	5428(2)	30(1)
C(51)	7041(3)	5480(2)	3340(2)	22(1)
C(52)	8198(3)	5044(2)	4067(2)	28(1)
C(53)	9596(3)	4336(2)	3912(2)	30(1)
C(54)	9868(3)	4053(2)	3026(2)	32(1)
C(55)	8713(3)	4463(2)	2306(2)	32(1)
C(56)	7313(3)	5156(2)	2470(2)	28(1)
C(61)	1302(3)	8796(2)	−1264(2)	24(1)
C(62)	1471(3)	8321(2)	−2042(2)	30(1)
C(63)	2384(3)	8649(3)	−2853(2)	37(1)
C(64)	3160(3)	9452(3)	−2897(2)	37(1)
C(65)	2998(3)	9939(2)	−2128(2)	34(1)
C(66)	2073(3)	9617(2)	−1326(2)	29(1)
C(71)	−1086(3)	7657(2)	−512(2)	23(1)
C(72)	−2260(3)	8261(2)	−1200(2)	28(1)
C(73)	−3312(3)	7778(2)	−1495(2)	30(1)
C(74)	−3213(3)	6699(2)	−1121(2)	29(1)
C(75)	−2089(3)	6096(2)	−422(2)	29(1)
C(76)	−1031(3)	6577(2)	−119(2)	26(1)

Table 5
Selected parameters from crystal structure analyses and calculated minimum geometries (in parentheses) [a]

	7a	**7c**	**7d**
P(1)–N (Å)	3.249 (3.323)	3.503 (3.425)	3.365 (3.383)
P(1)–P(2) (Å)	4.075 (3.741)		
Cp(1)–Cp(2) torsional angle (°)	6.1 (3.6)	6.2 (4.5)	5.3 (2.9)
Cp(1)–Cp(2) tilt angle (°)	13.0 (19.1)	9.4 (16.5)	11.5 (15.9)
Deviation from best Cp plane [b]			
C(21)–Cp(1) (Å)	−0.044	−0.070	−0.020
P(1)–Cp(1) (Å)	0.148	−0.093	−0.089
C(23)–Cp(2) (Å)	−0.157	−0.164	−0.135
P(2)–Cp(2) (Å)	0.429	−0.066	0.047

[a] See [11]; labeling scheme as given in Fig. 2.
[b] Positive values refer to deviations distal to iron, while negative values refer to deviations proximal to iron.

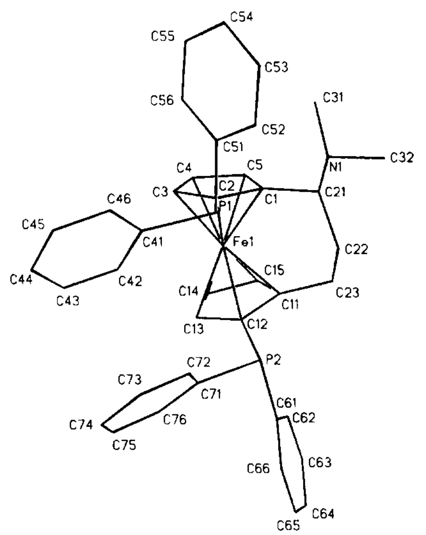


Fig. 2. The crystal structure of **7a**, together with the atom numbering used for the description of the crystal structures.

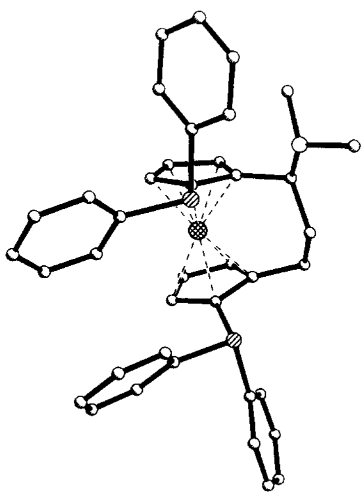


Fig. 3. Crystal structure of racemic **7a** (fraction 2; (*S*)-enantiomer shown). Hydrogen atoms have been omitted for clarity.

planes which range from 9.4 to 13.0°. Noticeable deviations from ideal geometry are observed for C(21) and C(23) which are shifted towards iron and for the phosphorus atoms in **7a** which are shifted to the distal side of the Cp planes.

Force field calculations were conducted for all aminodiphosphines in two conformations A and B which are interconvertible by a flip of the C_3 bridge (Fig. 6).

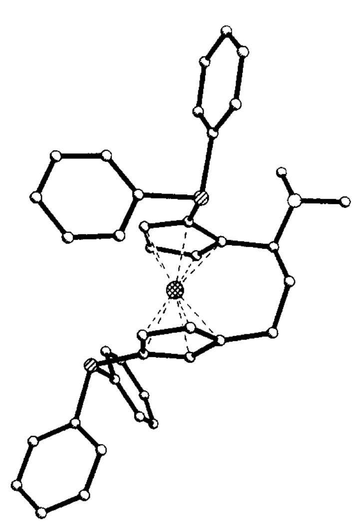


Fig. 4. Crystal structure of racemic **7c** (fraction 3)

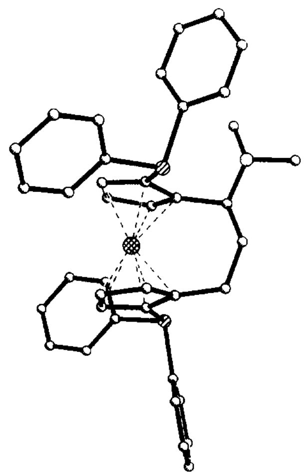


Fig. 5. Crystal structure of racemic **7d** (fraction 1).

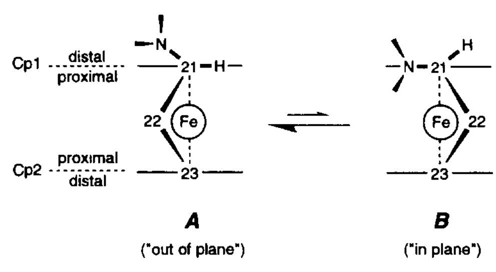


Fig. 6.

Table 6
MMX calculations for conformers of **7a**–**7d** and **11**

	7a	7b	7c	7d	11
$\Delta E_{in\text{-}out}$ [a] (kJ)	30.7	28.3	33.3	30.6	25.3
$(E_{7a\ out})-(E_{x\ out})$ [b] (kJ)	0	9.7	9.6	4.4	1.3

[a] Energy difference of conformers with dimethylamino substituent either in plane or out of plane of Cp(1); see Fig. 6.
[b] Energy differences arising from substitution pattern are calculated for the "out-of-plane" conformation (Fig. 6A); **7a** with highest energy was arbitrarily set equal to zero.

Energy differences between A and B are similar for **7a–7d** and **11** and high enough to exclude the population of B in detectable amounts. Only in the case of **11** was a somewhat smaller energy difference calculated which reflects a less pronounced steric interaction between PPh_2 and $N(CH_3)_2$. Energy differences arising from different substitution pattern are as expected for varying steric repulsions. So **7a** shows highest energy since it receives steric strain of two PPh_2 groups adjacent to the carbon bridge and directly opposed to each other. In contrast with this, **7b** and **7c** with a single $Ph_2P \cdots\cdots CHN(CH_3)_2$ contact show considerably lower energy. Good agreement with the crystal structures was found for torsional angles and tilt angles; in particular, trends are reproduced satisfactorily although tilt angles tend to be too large.

3. Conclusions

Our findings clearly demonstrate that dilithiation in ferrocenes takes place at the second Cp ring preferred opposite to the first Li atom. We believe that this arrangement is stabilized via lithium associates, possibly with participation of TMEDA since for the dilithio derivative of the non-bridged aminoferrocene **1** a corresponding structure was confirmed by X-ray analysis [13]. As a consequence of this, kinetic control favors the formation of **7a** despite of its significantly higher energy compared with isomers **7b–7d**. Compound **7a** is expected to function as a bidentate ligand in transition metal complexes, with either P–P or P–N coordination. The corresponding complexes will be tested for their efficiency in asymmetric catalysis.

4. Experimental part

The ^1H, ^{13}C and ^{31}P NMR (proton-decoupled) spectra were recorded in $CDCl_3$ on a Bruker AM-400 spectrometer at 400, 100 and 162 MHz respectively. Chemical shifts δ are given relative to tetramethylsilane (TMS) as internal standard (^1H and ^{13}C NMR) and relative to 85% H_3PO_4 (^{31}P NMR). ^{13}C NMR spectra were recorded in a J-modulated mode; J refers to phosphorus–carbon coupling constants. In spectral areas with extensive signal overlapping, multiplets could not be identified; these signals of unclear relationship are underlined, ignoring probable multiplet structures. Mass spectra were recorded on a Varian MAT-CH7. Optical rotations were measured with a Perkin–Elmer polarimeter 241 in CH_2Cl_2 at 20°C (thermostated). CD spectra were recorded on a dichrograph CD 6 (Jobin–Yvon) (CH_2Cl_2 at 20°C) and UV spectra were recorded on a Perkin–Elmer Lambda 7 spectrometer (CH_2Cl_2). Melting points were determined on a Kofler melting-point apparatus and are uncorrected. Elemental analyses were carried out at Mikroanalytisches Laboratorium der Universität Wien (J. Theiner). Diethyl ether and benzene were distilled from $LiAlH_4$ prior to use; chlorodiphenylphosphine (Aldrich) was distilled and stored under Ar. All the other chemicals were of analytical grade and used as purchased.

4.1. *(±)-1,1′-(1-N,N-Dimethylaminopropane-1,3-diyl)-ferrocene (5)*

This was prepared according to literature procedures [14]. The optical resolution of **5** was performed via fractional crystallization of the diastereomeric tartrates [15].

4.2. *Isomeric bis(diphenylphosphino)-1,1′-(1-N,N-dimethylaminopropane-1,3-diyl)ferrocenes (7a–7d and 11) and 2-diphenylphosphino-1,1′-(1-N,N-dimethylaminopropane-1,3-diyl)-ferrocene (6)*

The reaction was carried out in 100 ml Schlenk tubes under Ar. 1.00 g (3.71 mmol) of **5** was dissolved in 25 ml of absolute diethyl ether. The solution was degassed and 2.7 ml of a 1.6 N solution of n-BuLi in hexane (4.32 mmol) was added dropwise. After stirring for 3 h at room temperature, 1.35 ml (9.0 mmol) of N,N,N',N'-tetramethylethylenediamine and 8.1 ml of n-BuLi in hexane (13.0 mmol) were added in portions. The mixture was stirred at room temperature for 20 h. The dark-red solution was cooled to −78°C, and 3.65 ml (19.8 mmol) of chlorodiphenylphosphine was added. After warming to room temperature the mixture was refluxed for 1 h. The reaction was quenched by careful addition of 10 ml of Na_2CO_3 solution (10%). The organic layer was separated and the aqueous layer was extracted twice with 10 ml of diethyl ether. The combined extracts were dried with $MgSO_4$ and the solvent was removed in vacuo to give 3.8 g of a red wax. The crude mixture was chromatographed on silica gel (40–63 μm; column, 3 × 90 cm) using petroleum ether : ethylacetate : triethylamine (75 : 24.5 : 0.5) for packing. Elution with a solvent gradient petroleum ether : ethylacetate : triethylamine (75 : 24.7 : 0.3 → 65 : 34.8 : 0.2) afforded the following fractions (in the order of elution).

4.2.1. *Fraction 1: (±)-2,5′-bis(diphenylphosphino)-1,1′-(1-N,N-dimethylaminopropane-1,3-diyl)-ferrocene (7d)*

Yield, 161 mg (6.8%); melting point (m.p.), above 170°C (decomposition). ^1H NMR: δ 1.86 (6H, s), 2.35 (1H, br. t, J = 12 Hz), 2.43 (2H, m), 2.67 (1H, br. d, J = 10.6 Hz), 2.98 (1H, br. q, J = 12 Hz), 3.34 (1H, s), 3.59 (1H, br.s), 3.75 (1H, m), 3.84 (1H, m), 4.43 (1H, br.s), 4.67 (1H, br.s), 7.15–7.36 (16H, m), 7.36–7.46 (4H, m) ppm. ^{13}C NMR: δ 23.63 (CH_2, d, J = 11.7 Hz), 38.39 (CH_2, d, J = 9.1 Hz), 44.34 (CH_3, s), 66.23

(CH, s), 69.89 (CH, s), 71.35 (CH, s), 71.91 (CH, d, $J = 4$ Hz), 73.93 (CH, d, $J = 4$ Hz), 74.88 (CH, m), 75.83 (C, d, $J = 12$ Hz), 78.28 (C, d, $J = 3$ Hz), 79.63 (CH, m), 92.18 (C, d, $J = 20.2$ Hz), 93.56 (C, d, $J = 22.1$ Hz), 127.57 (CH, d, $J = 7.5$ Hz), 127.72 (CH, d, $J = 6.8$ Hz), 127.76 (CH, s), 127.96 (CH, s), 128.06 (CH, d, $J = 7.6$ Hz), 128.20 (CH, d, $J = 7$ Hz), 128.23 (CH, s), 128.93 (CH, s), 132.26 (CH, d, $J = 18$ Hz), 133.42 (CH, d, $J = 20$ Hz), 134.30 (CH, d, $J = 20$ Hz), 134.59 (CH, d, $J = 20$ Hz), 137.00 (C, d, $J = 10$ Hz), 138.70 (C, d, $J = 12$ Hz), 139.21 (C, d, $J = 16$ Hz), 139.30 (C, d, $J = 17$ Hz) ppm. ^{31}P NMR: δ −22.09 (s), −21.79 (s) ppm. MS (250°C): m/z (relative %) 638 M+ (100), 623 (49), 594 (23), 560 (12), 515 (5), 452 (25), 408 (34), 331 (44), 329 (25), 319 (52). UV ($c = 6.04 \times 10^{-2}$ and 1.2×10^{-3} mol^{-1}): $\lambda_{max}(\varepsilon)$ 255 (22100), 437 (257) nm. Anal. Found: C, 73.02; H, 5.85; N, 2.31; P, 9.52; $C_{39}H_{37}FeNP_2$ calc.: C, 73.48; H, 5.85; N, 2.20; P, 9.72%. When the reaction was carried out with (−)(*S*)-**5**, (−)(S_c)(S_{m1})(S_{m2})-**7d** was obtained: $[\alpha]_D^{20} = -208°$ ($c = 0.385$).

4.2.2. Fraction 2: (±)-2,2′-bis(diphenylphosphino)-1,1′-(1-N,N-dimethylaminopropane-1,3-diyl)ferrocene (7a)

Yield, 1034 mg (43.6%); m.p., above 172°C (decomposition). ^{1}H NMR: δ 1.61 (6H, s), 1.74 (1H, br. t, $J = 14$ Hz), 1.93 (1H, br. d, $J = 14.9$ Hz), 2.22 (1H, br. d, $J = 13.5$ Hz), 2.33 (1H, br. d, $J = 11.1$ Hz), 3.37 (1H, br. q, $J = 13$ Hz), 4.07 (1H, br.s), 4.14 (2H, br.s), 4.22 (1H, t, $J = 2.5$ Hz), 4.26 (1H, t, $J = 2.5$ Hz), 4.28 (1H, br.s), 6.84 (2H, t, $J = 7.5$ Hz), 7.06 (3H, m), 7.21 (7H, m), 7.33 (2H, t, $J = 7.5$ Hz), 7.43 (6H, m) ppm. ^{13}C NMR: δ 25.95 (CH$_2$, s), 38.76 (CH$_2$, t, $J = 8.2$ Hz), 43.95 (CH$_3$, s), 66.87 (CH, s), 67.51 (CH, s), 68.44 (CH, s), 73.13 (CH, d, $J = 5.4$ Hz), 73.73 (CH, br. d, $J = 3.1$ Hz), 73.85 (CH, s), 74.33 (CH, s), 78.05 (C, d, $J = 18.4$ Hz), 80.45 (C, d, $J = 12.7$ Hz), 91.73 (C, dd, $J = 8.2$, 1.9 Hz), 92.14 (C, dd, $J = 15.1$, 3.7 Hz), 126.36 (CH, s), 127.21 (CH, d, $J = 3.7$ Hz), 127.35 (CH, d, $J = 7.6$ Hz), 127.74 (CH, d, $J = 6.8$ Hz), 127.78 (CH, s), 128.11 (CH, d, $J = 7.6$ Hz), 128.24 (CH, s), 128.65 (CH, s), 133.08 (CH, dd, $J =$ 13.7, 3.8 Hz), 133.29 (CH, dd, $J = 19.8$, 2.3 Hz), 134.98 (CH, dd, $J = 19.9$, 3.0 Hz), 135.73 (CH, dd, $J = 20.6$, 2.3 Hz), 137.98 (C, d, $J = 11$ Hz), 139.99 (C, d, $J = 15$ Hz), 140.40 (C, d, $J = 12$ Hz), 140.67 (C, d, $J = 10$ Hz) ppm. ^{31}P NMR: δ −24.30 (d, $J = 43.5$ Hz), −24.77 (d, $J = 43.9$ Hz) ppm. MS (200°C): m/z (relative %) 638 M+ (60), 595 (13), 560 (5), 517 (13), 453 (14), 409 (29), 408 (27), 331 (49). UV ($c = 1.72 \times 10^{-2}$ and 3.4×10^{-4} moll^{-1}): $\lambda_{max}(\varepsilon)$ 255 sh (24100), 447 (425) nm. Anal. Found: C, 73.02; H, 5.83; N, 2.13; P, 9.77. $C_{39}H_{37}FeNP_2$ Calc.: C, 73.48; H, 5.85; N, 2.20; P, 9.72%. When the reaction was carried out with (−)(*S*)-**5**, (−)(S_c)(S_{m1})(R_{m2})-**7a** was obtained: $[\alpha]_D^{20} = -235°$ ($c = 0.109$).

4.2.3. Fraction 3: (±)-2,4′-bis(diphenylphosphino)-1,1′-(1-N,N-dimethylaminopropane-1,3-diyl)ferrocene (7c)

Yield, 113 mg (4.8%); m.p., 194–198°C (decomposition). ^{1}H NMR: δ 1.78 (6H, s), 1.85 (1H, br. t, $J = 14$ Hz), 2.38 (2H, br. d, $J = 9$ Hz), 2.63 (1H, br. d, $J = 15$ Hz), 2.91 (1H, br. q, $J = 13$ Hz), 3.53 (1H, br.s), 3.56 (1H, br.s), 4.11 (1H, t, $J = 1.5$ Hz), 4.13 (1H, m), 4.17 (1H, t, $J = 2.3$ Hz), 4.56 (1H, br.s), 7.14–7.38 (20H, m) ppm. ^{13}C NMR: δ 25.55 (CH$_2$, s), 38.23 (CH$_2$, d, $J = 9.4$ Hz), 44.26 (CH$_3$, s), 66.31 (CH, d, $J = 2$ Hz), 73.00 (CH, d, $J = 2.9$ Hz), 74.56 (CH, dd, $J = 6.3$, 3 Hz), 74.84 (CH, d, $J = 4.8$ Hz), 74.99 (CH, d, $J = 4.5$ Hz), 75.08 (CH, d, $J = 10.3$ Hz), 76.00 (C, d, $J = 6.8$ Hz), 76.28 (C, d, $J = 14.3$ Hz), 76.40 (CH, d, $J = 19.5$ Hz), 91.50 (C, d, $J = 4.8$ Hz), 91.87 (C, m), 127.53 (CH, d, $J = 7.3$ Hz), 127.64 (CH, d, $J = 6.3$ Hz), 127.74 (CH, s), 127.84 (CH, d, $J = 6.7$ Hz), 128.07 (CH, d, $J = 6.8$ Hz), 128.12 (CH, s), 128.22 (CH, s), 128.33 (CH, s), 133.05 (CH, d, $J = 19$ Hz), 133.19 (CH, d, $J = 19$ Hz), 133.47 (CH, d, $J = 20$ Hz), 133.91 (CH, d, $J = 19$ Hz), 138.55 (C, d, $J = 11.4$ Hz), 138.65 (C, d, $J = 8$ Hz), 139.10 (C, d, $J = 9.8$ Hz), 139.27 (C, d, $J = 8.5$ Hz) ppm. ^{31}P NMR: δ −16.68 (s), −21.61 (s) ppm. MS (240°C); m/z (relative %) 638 M+ (83), 594 (23), 593 (22), 409 (31), 408 (42), 407 (21), 331 (39). UV ($c = 1.81 \times 10^{-2}$ and 3.63×10^{-4} moll^{-1}): $\lambda_{max}(\varepsilon)$ 253 (24200), 437 (398) nm. Anal. Found: C, 73.16; H, 6.09; N, 2.04; P, 9.77. $C_{39}H_{37}FeNP_2$ Calc.: C, 73.48; H, 5.85; N, 2.20; P, 9.72%. When the reaction was carried out with (−)(*S*)-**5** the (−)(S_c)(S_{m1})(S_{m2})-**7c** was obtained: $[\alpha]_D^{20} = -47°$ ($c = 0.116$).

4.2.4. Fraction 4: (±)-2,3′-bis(diphenylphosphino)-1,1′-(1-N,N-dimethylaminopropane-1,3-diyl)ferrocene (7b)

Yield, 150 mg (6.3%); m.p., above 145°C (decomposition). ^{1}H NMR: δ 1.79 (6H, s), 1.94 (1H, br. t, $J = 14$ Hz), 2.37 (1H, br. d, $J = 13$ Hz), 2.42 (1H, br. d, $J = 12$ Hz), 2.64 (1H, br. d, $J = 14$ Hz), 3.26 (1H, br. q, $J = 14$ Hz), 3.46 (1H, m), 3.76 (1H, t, $J = 2.5$ Hz), 3.85 (1H, br.s), 4.08 (1H, br.s), 4.23 (1H, br.s), 4.60 (1H, br.s), 7.03 (2H, m), 7.10 (2H, m), 7.18 (2H, m), 7.22 (7H, m), 7.28 (2H, m), 7.36 (1H, m), 7.44 (2H, br.t, $J = 7.5$ Hz), 7.65 (2H, br.t, $J = 7.5$ Hz) ppm. ^{13}C NMR: δ 25.74 (CH$_2$, s), 38.64 (CH$_2$, d, $J = 13.6$ Hz), 44.26 (CH$_3$, s), 66.81 (CH, d, $J = 2$ Hz), 69.03 (CH, s), 69.74 (CH, d, $J = 5$ Hz), 74.37 (CH, d, $J = 4$ Hz), 74.65 (CH, s), 76.73 (CH, s), ~77.38 (CH), 78.48 (C, d, $J = 17$ Hz), 79.67 (C, d, $J = 15$ Hz), 90.56 (C, dd, J = 17.7, 2.5 Hz), 91.70 (C, d, $J = 9$ Hz), 127.45, 127.47, 127.51, 127.52, 127.58, 127.60 (4 × CH), 127.92 (CH, d, $J = 5.4$ Hz), 128.26 (CH, s), 128.36 (CH, s), 128.58 (CH, dd, $J = 7.0$, 2.4 Hz), 132.20 (CH, d, $J = 18$ Hz), 133.46 (CH, d, $J = 20$ Hz), 134.12 (CH, d, $J = 20$ Hz), 135.22 (CH, dd, $J = 20$, 4.5 Hz), 137.86 (C, d, $J = 9$ Hz), 138.67 (C, d, $J = 12$ Hz), 139.93 (C, d, $J = 8$ Hz), 140.80 (C, d, $J = 13$ Hz) ppm. ^{31}P NMR: δ −20.10 (s), −21.70 (s). MS (240°C): m/z (relative %) 638 M+ (100), 594 (28), 593 (31), 592 (30), 560 (4), 517 (7), 452 (7), 409 (27), 408 (25), 407 (14), 331 (20), UV ($c = 1.76 \times 10^{-2}$ and 3.51×10^{-4} mol l^{-1}): $\lambda_{max}(\varepsilon)$ 255 (23900), 453 (327) nm. Anal. Found: C, 73.18; H, 5.96; N, 1.97; P, 9.94. $C_{39}H_{37}FeNP_2$ Calc.: C, 73.48; H, 5.85; N, 2.20; P, 9.72%. When the reaction was carried out with (−)(S)-**5**, (+)(S_c)(S_{m1})(R_{m2})-**7b** was obtained: $[\alpha]_D^{20} = +446°$ ($c = 0.0224$).

*4.2.5. Fraction 5: (±)-5,5′-bis(diphenylphosphino)-1,1′-(1-N,N-dimethylaminopropane-1,3-diyl)ferrocene (**11**)*

Yield, 50 mg (2.1%); oil. ^{1}H NMR: δ 1.85 (6H, s), 2.03 (1H, m), 2.13 (1H, m), 2.16 (1H, m), 2.48 (1H, m), 3.18 (1H, br. s), 3.94 (1H, br.s), 4.13 (1H, br.s), 4.31 (1H, t, J = 2.5 Hz), 4.36 (1H, t, J = 2.5 Hz), 4.37 (1H, br.s), 4.54 (1H, br.s), 6.95 (2H, td, J = 7, 2 Hz), 7.00–7.61 (16H, m), 7.71 (2H, m) ppm. ^{13}C NMR: δ 23.05 (CH_2, s), 38.82 (CH_2, s), 43.58 (CH_3, s), 60.96 (CH, d, J = 7.2 Hz), 69.12 (CH, s), 69.62 (CH, s), 70.88 (CH, s), 71.08 (CH, br.s), 72.58 (2 × CH, br.s), 79.37 (C, d, J = 12 Hz), 82.67 (C, d, J = 10 Hz), ~87.3 (C, m), 90.42 (C, d, J = 15 Hz), 127.50 (CH, d, J = 7.4 Hz), 127.60 (CH, s), 127.78 (CH, d, J = 7.4 Hz), 128.04, 128.11, 128.17, 128.41, 128.67 (5 × CH), 133.10 (CH, d, J = 20 Hz), 133.80 (CH, dd, J = 17, 2.5 Hz), 134.66 (CH, d, J = 22 Hz), 135.05 (CH, d, J = 20 Hz), 137.64 (C, m), 139.36 (C, d, J = 13 Hz), 140.17 (C, d, J = 14 Hz) ppm. ^{31}P NMR: δ −25.01 (d, J = 48.4 Hz), −26.48 (d, J = 48.4 Hz) ppm. MS (200°C): m/z (relative %) 638 M+ (9), 623 (7), 560 (3), 452 (4), 386 (10), 331 (7). UV ($c = 1.59 \times 10^{-2}$ and 3.2×10^{-4} mol l^{-1}): [$\lambda_{max}(\varepsilon)$] 253 sh (19500), 451 (308) nm.

When the reaction was carried out with (−)(S)-**5**, (+) (S_c)(R_{m1})(S_{m2})-**11** was obtained: $[\alpha]_D^{20} = +60°$ ($c = 0.101$).

*4.2.6. Fraction 6: (±)-2-diphenylphosphino-1,1′-(1-N,N-dimethylaminopropane-1,3-diyl)ferrocene (**6**)*

Yield, 334 mg (19.8%); m.p., 168–172°C; spectral properties were found to be identical with those of an authentic sample.

*4.3. Bis(diphenylphosphino)-1,1′-(1-acetoxypropane-1,3-diyl)ferrocenes (**8a–8d**) from corresponding bis(diphenylphosphino)-1,1′-(1-N,N-dimethylaminopropane-1,3-diyl)-ferrocenes (**7a–7d**) (general procedure)*

The aminodiphosphine **7** and freshly distilled acetic anhydride were mixed in a small Schlenk tube, degassed and heated to about 100°C. During the course of the reaction, the amine dissolved. After completion of the reaction (TLC) the excess of anhydride was removed in vacuo and the residue was chromatographed on a short column (silica gel; 1 × 20 cm) with petroleum ether : ethylacetate (75 : 25). Different reaction conditions were applied to isomers **7a–7d** as specified below:

*4.3.1. (±)-2,2′-Bis(diphenylphosphino)-1,1′-(1-acetoxypropane-1,3-diyl)ferrocene (**8a**)*

450 mg (0.70 mmol) of **7a** were heated to 100°C for 2 h; yield, 430 mg (94%). ^{1}H NMR: δ 1.06 (3H, s), 1.89 (2H, m), 2.01 (1H, m), 3.74 (1H, m), 3.94 (2H, br.s), 4.13 (1H, t, J = 2 Hz), 4.32 (1H, t, J = 2.4 Hz), 4.37 (1H, br.s), 4.51 (1H, br.s), 5.35 (1H, br.d, J = 9.8 Hz), 7.00 (2H, t, J = 7.3 Hz), 7.04–7.30 (14H, m), 7.38–7.49 (4H, m) ppm. ^{13}C NMR: δ 19.73 (CH_3, s), 24.71 (CH_2, s), 40.58 (CH_2, dd, J = 9.1, 7.6 Hz), 67.36 (CH, s), 69.42 (CH, s), 73.47 (CH, s), 73.70 (CH, d, J = 3.8 Hz), 73.83 (CH, d, J = 3.8 Hz), ~74.11 (2 × CH, m), 80.33 (C, dd, J = 18.3, 2 Hz), 80.46 (C, d, J = 13.8 Hz), 84.09 (C, d, J = 16.8 Hz), 91.60 (C, d, J = 11.4 Hz), 127.76 (CH, d, J = 6.9 Hz), 127.77 (CH, s), 127.81 (CH, d, J = 6.8 Hz), 128.05 (CH, d, J = 6.8 Hz), 128.09 (CH, s), 128.22 (CH, s), 128.33 (CH, d, J = 7.7 Hz), 128.78 (CH, s), 132.95 (CH, d, J = 19.9 Hz), 133.98 (CH, d, J = 22.1 Hz), 134.30 (CH, d, J = 19.8 Hz), 134.83 (CH, dd, J = 18.3, 3.1 Hz), 137.59 (C, d, J = 13 Hz), 137.99 (C, d, J = 14.5 Hz), 138.53 (C, d, J = 15.2 Hz), 140.90 (C, d, J = 12.2 Hz), 170.75 (C, s) ppm. ^{31}P NMR: δ −23.45 (d, J = 41.0 Hz), −26.59 (d, J = 41.0 Hz) ppm. MS (240°C): m/z (relative %) 653 M+ (100), 610 (11), 593 (5), 575 (15), 515 (11), 467 (15), 424 (18), 407 (41).

*4.3.2. (±)-2,3′-Bis(diphenylphosphino)-1,1′-(1-acetoxypropane-1,3-diyl)ferrocene (**8b**)*

245 mg (0.38 mmol) of **7b** were heated to 100°C for 2 h; yield, 187 mg (73%). ^{1}H NMR: δ 1.14 (3H, s), 2.17 (2H, m), 2.63 (1H, br.d, J = 14.7 Hz), 3.56 (3H, m), 3.76 (1H, t, J = 2.4 Hz), 4.36 (2H, s), 4.75 (1H, s), 5.32 (1H, dd, J = 11.3, 2.9 Hz), 6.93 (2H, t, J = 6.9 Hz), 7.08–7.19 (6H, m), 7.20–7.30 (7H, m), 7.41–7.53 (3H, m), 7.60 (2H, td, J = 7.9, 1.5 Hz) ppm. ^{13}C NMR: δ 19.87 (CH_3, s), 24.38 (CH_2, s), 40.17 (CH_2, d, J = 13 Hz), 69.79 (CH, s), 69.94 (CH, d, J = 5.4 Hz), 73.47 (CH, s), 73.82 (CH, d, J = 3.8 Hz), 74.54 (CH, s), 76.95 (CH, m), 78.39 (CH, dd, J = 32.9, 5 Hz), 79.36 (C, d, J = 16 Hz), 79.75 (C, d, J = 14.5 Hz), 84.41 (C, d, J = 16.8 Hz), 91.33 (C, d, J = 6.9 Hz), 127.47 (CH, s), 127.58 (CH, d, J = 7.4 Hz), 127.92 (CH, s), 127.94 (CH, d, J = 5.3 Hz), 128.07 (CH, d, J = 6.9 Hz), 128.47 (CH, s), 128.68 (CH, dd, J = 7.6, 2.2 Hz), 128.95 (CH, s), 131.98 (CH, d, J = 17.6 Hz), 132.75 (CH, d, J = 19.8 Hz), 134.21 (CH, d, J = 20.6 Hz), 135.70 (CH, dd, J = 20.6, 3.8 Hz), 136.29 (C, d, J = 9.9 Hz), 138.30 (C, d, J = 10.4 Hz), 140.00 (C, d, J = 9.9 Hz), 140.71 (C, d, J = 13 Hz), 170.19 (C, s) ppm. ^{31}P NMR: δ −19.92 (s), −20.92 (s) ppm. MS

(240°C): m/z (relative %) 653 M + (100), 610 (14), 595 (3), 576 (1), 515 (2), 467 (4), 424 (24), 407 (12).

*4.3.3. (±)-2,4'-Bis(diphenylphosphino)-1,1'-(1-acetoxy-propane-1,3-diyl)ferrocene (**8c**)*

122 mg (0.19 mmol) of **7c** were heated to 100°C for 2 h; yield, 85 mg (68%). ^{1}H NMR: δ 1.14 (3H, s), 2.05 (1H, br. t, $J = 14$ Hz), 2.23 (1H, m), 2.62 (1H, br. d, $J = 14.7$ Hz), 3.27 (1H, br. q, $J = 13$ Hz), 3.33 (1H, br.s), 3.70 (1H, br.s), 4.20 (2H, m), 4.40 (1H, m), 4.72 (1H, br.s), 5.27 (1H, dd, $J = 11.3$, 3.3 Hz), 7.12–7.34 (20H, m) ppm. ^{13}C NMR: δ 19.83 (CH_3, s), 24.34 (CH_2, s), 39.61 (CH_2, d, $J = 10.7$ Hz), 73.22 (CH, s), 73.88 (CH, d, $J = 3.0$ Hz), 74.64 (CH, d, $J = 3.8$ Hz), 74.73 (CH, d, $J = 3.8$ Hz), 75.02 (CH, d, $J = 12.2$ Hz), 75.13 (CH, dd, $J = 7$, 3 Hz), 76.38 (CH, d, $J = 18.2$ Hz), 76.50 (C, d, $J = 7$ Hz), 77.41 (C, d, $J = 13.7$ Hz), 85.17 (C, d, $J = 18.2$ Hz), 91.31 (C, d, $J = 4.6$ Hz), 127.83 (CH, d, $J = 6.8$ Hz), 127.93 (CH, d, $J = 6.8$ Hz), 128.08 (CH, s), 128.11 (2 × CH, d, $J = 6.1$ Hz), 128.25 (CH, s), 128.46 (CH, s), 128.77 (CH, s), 132.80 (CH, d, $J = 19.1$ Hz), 132.94 (CH, d, $J = 19.1$ Hz), 133.18 (CH, d, $J = 19.2$ Hz), 134.06 (CH, d, $J = 19.1$ Hz), 136.89 (C, d, $J = 9.9$ Hz), 138.45 (C, d, $J = 9.1$ Hz), 138.67 (C, d, $J = 9.9$ Hz), 138.96 (C, d, $J = 9.9$ Hz), 170.49 (C, s) ppm. ^{31}P NMR: δ −17.06 (s), −20.66 (s) ppm. MS (240°C): m/z (relative %): 653 M + (100), 610 (10), 595 (3), 576 (2), 515 (2), 467 (3), 424 (32), 407 (13).

*4.3.4. (±)-2,5'-Bis(diphenylphosphino)-1,1'-(1-acetoxy-propane-1,3-diyl)ferrocene (**8d**)*

129 mg (0.20 mmol) of **7d** were heated to 90°C for 2 h; yield, 97 mg (74%) of **8d** as a mixture of diastereoisomers (approximately 30 : 70). The crude product was used without further purification.

*4.4. (±)-2,3'-Bis(diphenylphosphino)-1,1'-(propane-1,3-diyl)ferrocene (**10b**)*

80 mg (0.60 mmol) of $AlCl_3$ and 200 mg (5.3 mmol) of $LiAlH_4$ were mixed with 2 ml of anhydrous diethyl ether. A solution from 80 mg (0.12 mmol) of **8b** in 4 ml of diethylether : benzene (1 : 1) was added to the $AlCl_3$–$LiAlH_4$ suspension with cooling. After stirring the mixture at room temperature for 100 h, the reaction was quenched by careful addition of water. The organic layer was separated and the aqueous layer was extracted with 3 × 10 ml of methylene chloride. The combined extracts were dried with $MgSO_4$ and evaporated. Chromatography on silica gel with petroleum ether : chloroform (50 : 50) afforded **10b** as an oil; yield, 12 mg (19%). ^{1}H NMR: δ 1.93 (2H, m), 2.07 (1H, m), 2.22 (1H, m), 2.38 (1H, m), 3.42 (1H, br.s), 3.60 (1H, br.s), 3.67 (1H, t, $J = 2.5$ Hz), 4.06 (1H, br.s), 4.11 (1H, br.s), 4.45 (1H, br.s), 7.04–7.11 (2H, m), 7.12–7.35 (14H, m), 7.37–7.50 (2H, m), 7.55–7.63 (2H, m) ppm. ^{13}C NMR: δ 22.78 (CH_2, d, $J = 7.6$ Hz), 24.21 (CH_2, s), 34.85 (CH_2, d, $J = 3.8$ Hz), 69.16 (CH, s), 70.92 (CH, d, $J = 4.5$ Hz), 71.44 (CH, s), 71.51 (CH, d, $J = 3.1$ Hz), 74.87 (CH, s), 77.89 (C, d, $J = 12.2$ Hz), 79.42 (C, d, $J = 6.1$ Hz), 82.27 (CH, dd, $J = 36.6$, 6.9 Hz), 88.77 (C, d, $J = 8.4$ Hz), 90.05 (C, d, $J = 19.1$ Hz), 127.40 (CH, s), 127.54 (CH, d, $J = 6.8$ Hz), 127.93 (CH, d, $J = 5.5$ Hz), 128.05 (CH, s), 128.18 (CH, d, $J = 6.2$ Hz), 128.34 (CH, s), 128.52 (CH, dd, $J = 7.6$, 1 Hz), 128.87 (CH, s), 132.06 (CH, d, $J = 17.6$ Hz), 132.63 (CH, d, $J = 19.1$ Hz), 134.30 (CH, d, $J = 20.5$ Hz), 135.40 (CH, dd, $J = 20.6$, 4.2 Hz), 136.38 (C, d, $J = 9.9$ Hz), 138.86 (C, d, $J = 10.6$ Hz), 139.26 (C, d, $J = 12.2$ Hz), 141.09 (C, d, $J = 13$ Hz) ppm. ^{31}P NMR: δ −18.85 (s), −20.60 (s) ppm. MS (200°C): m/z (relative %) 595 M + (62), 518 (9), 486 (2), 410 (100), 333 (25), 331 (26).

*4.5. Hydroxy derivatives **9a**, **9b** and **9d** (general procedure)*

The acetate **8** was suspended in anhydrous diethyl ether and $LiAlH_4$ was added. After stirring at room temperature for 1 h, the mixture was quenched with excess of water. The organic layer was separated and the aqueous layer was extracted with three 10 ml portions of ether. The combined extracts were dried with $MgSO_4$ and chromatographed on silicagel with petroleum ether : ethyl acetate (75 : 25). The products isolated from the chromatography were used without further purification for the preparation of hydrocarbons **10**.

*4.5.1. (±)-2,2'-Bis(diphenylphosphino)-1,1'-(1-hydroxy-propane-1,3-diyl)ferrocene (**9a**)*

210 mg (0.32 mmol) of **8a** and 19 mg (0.50 mmol) of $LiAlH_4$ in 20 ml of ether yielded 181 mg (92%) of **9a**. ^{1}H NMR: δ 1.93 (1H, m), 2.02 (1H, m), 2.15 (1H, m), 2.71 (1H, ddd, $J = 10.1$, 5.5, 3.5 Hz), 3.83 (1H, m), 3.66 (1H, t, $J = 2$ Hz), 4.06 (1H, m), 4.17 (1H, m), 4.19 (1H, t, $J = 2.5$ Hz), 4.28 (1H, m), 4.32 (1H, t, $J = 2.5$ Hz), 4.38 (1H, br. t, $J = 8$ Hz), 6.97–7.07 (4H, m), 7.11–7.43 (14H, m) 7.63–7.72 (2H, m) ppm. ^{13}C NMR: δ 19.05 (CH_2, d, $J = 6.4$ Hz), 42.06 (CH_2, d, $J = 3$ Hz), 67.47 (CH, s), 68.89 (CH, s), 69.23 (CH, s), 71.43, 71.65, 71.67, 71.69 (2 × CH), 73.72 (CH, d, $J = 2.3$ Hz), 80.02 (C, d, $J = 7.9$ Hz), 80.41 (C, d, $J = 17.6$ Hz), 89.72 (C, d, $J = 10.7$ Hz), 89.87 (C, d, $J = 16.8$ Hz), 127.57 (CH, d, $J = 6.9$ Hz), 127.60 (CH, s), 128.08 (CH, d, $J = 7.6$ Hz), 128.17 (CH, s), 128.20 (CH, d, $J = 6.1$ Hz), 128.29 (CH, d, $J = 6.9$ Hz), 128.40 (CH, s), 128.95 (CH, s), 132.72 (CH, d, $J = 19.8$ Hz), 133.49 (CH, d, $J = 20.6$ Hz), 133.66 (CH, d, $J = 15.3$ Hz), 135.91 (CH, dd, $J = 19.8$, 2.2 Hz), 136.36 (C, d, $J = 9.9$ Hz), 138.60 (C, d, $J = 16$ Hz), 139.75

(C, d, $J = 13$ Hz), 139.83 (C, dd, $J = 12.2$, 1.5 Hz) ppm. ^{31}P NMR: δ −23.11 (d, $J = 52.0$ Hz), −26.83 (d, $J = 52.0$ Hz) ppm. MS (240°C): m/z (relative %) 611 M + (100), 533 (21), 425 (30), 409 (36), 348 (40).

*4.5.2. (±)-2,3′-Bis(diphenylphosphino)-1,1′-(1-hydroxypropane-1,3-diyl)ferrocene (**9b**)*

93 mg (0.14 mmol) of **8b** and 22 mg (0.57 mmol) of $LiAlH_4$ in 10 ml of diethyl ether yielded 68 mg (78%) of **9b**. ^{1}H NMR: δ 2.12 (2H, br. m), 2.51 (1H, m), 3.25 (1H, br. q, $J = 10$ Hz), 3.51 (1H, br.s), 3.54 (1H, br.s), 3.71 (1H, t, $J = 2.5$ Hz), 4.16 (1H, s), 4.25 (1H, br.s), 4.33 (1H, m), 4.66 (1H, br.s), 6.97 (2H, t, $J = 7$ Hz), 7.07–7.16 (4H, m), 7.18–7.29 (9H, m), 7.39–7.51 (3H, m) 7.62 (2H, td, $J = 7.8$, 1.5 Hz) ppm. ^{13}C NMR: δ 23.12 (CH_2, s), 43.19 (CH_2, d, $J = 9.8$ Hz), 69.71 (CH, s), 70.07 (CH, d, $J = 5.2$ Hz), 70.62 (CH, s), 72.72 (CH, d, $J = 3.6$ Hz), 73.62 (CH, s), 76.61 (CH, dd, $J = 2$, 2 Hz), 78.85 (C, d, $J = 14.4$ Hz), 79.23 (C, d, $J = 13.8$ Hz), 79.61 (CH, dd, $J = 36$, 5.7 Hz), 88.81 (C, d, $J = 15.3$ Hz), 91.44 (C, d, $J = 7.5$ Hz), 127.50 (CH, s), 127.58 (CH, d, $J = 7.2$ Hz), 127.96 (CH, d, $J = 5.4$ Hz), 128.38, 128.40, 128.43, 128.46 (3 × CH), 128.67 (CH, dd, $J = 7.6$, 1.3 Hz), 129.09 (CH, s), 132.05 (CH, d, $J = 17.9$ Hz), 132.76 (CH, d, $J = 19.2$ Hz), 134.21 (CH, d, $J = 20.5$ Hz), 135.66 (CH, dd, $J = 20.8$, 4.2 Hz), 136.23 (C, d, $J = 10.2$ Hz), 138.46 (C, d, $J = 11.5$ Hz), 140.19 (C, d, $J = 10.6$ Hz), 140.72 (C, d, $J = 12.9$ Hz) ppm. ^{31}P NMR: δ −19.70 (s), −19.82 (br.s) ppm. MS (230°C): m/z (relative %): 611 M + (100), 533 (11), 425 (24), 409 (33), 347 (16), 305 (6).

*4.5.3. (±)-2,5′-Bis(diphenylphosphino)-1,1′-(1-hydroxypropane-1,3-diyl)ferrocene (**9d**)*

100 mg (0.15 mmol) of **8d** (m.d.) and 26 mg (0.68 mmol) of $LiAlH_4$ in 30 ml of ether yielded 70 mg (76%) of **9d** as a mixture of diastereomers.

*4.5.4. (±)-2,4′-Bis(diphenylphosphino)-1,1′-(1-hydroxypropane-1,3-diyl)ferrocene (**9c**)*

80 mg (0.12 mmol) of **8c**, dissolved in 4 ml of a mixture of diethyl ether : benzene (50 : 50), was added under cooling to a suspension from 64 mg (0.48 mmol) of $AlCl_3$ and 200 mg (5.27 mmol) of $LiAlH_4$ in 2 ml of diethyl ether. After stirring at room temperature for 100 h, the reaction was quenched with water. The organic layer was separated and the aqueous layer was extracted with 3 × 10 ml of methylene chloride. The combined extracts were dried with $MgSO_4$ and evaporated. The crude product was chromatographed on silicagel with petroleum ether : chloroform (50 : 50) to give 55 mg (75%) of **9c**; no trace of the hydrocarbon **10c** could be observed. ^{1}H NMR: δ 2.01 (1H, br. t, $J = 13$ Hz), 2.23 (1H, m), 2.52 (1H, ddd, $J = 15$, 5.9, 2.5 Hz), 3.06 (1H, br. q, $J = 12$ Hz), 3.40 (1H, m), 3.60 (1H, m), 4.15 (1H, m), 4.19 (1H, t, $J = 2.4$ Hz), 4.24 (1H, m), 4.33 (1H, dd, $J = 10$, 3 Hz), 4.61 (1H, br.s), 7.14–7.37 (20H, m) ppm. ^{13}C NMR: δ 23.56 (CH_2, s), 43.05 (CH_2, d, $J = 8.6$ Hz), 70.81 (CH, s), 73.75 (CH, d, $J = 4.6$ Hz), 73.87 (CH, d, $J = 3.1$ Hz), 74.53 (CH, d, $J = 10.2$ Hz), 74.60 (CH, d, $J = 4.5$ Hz), 75.77 (CH, m), 75.91 (CH, d, $J = 19.1$ Hz), 76.38 (C, d, $J = 7.6$ Hz), 76.69 (C, d, $J = 13.0$ Hz), 89.48 (C, d, $J = 18.5$ Hz), 91.75 (C, d, $J = 4.5$ Hz), 127.85 (CH, d, $J = 6.8$ Hz), 127.99 (CH, d, $J = 6.8$ Hz), 128.10 (CH, d, $J = 6.1$ Hz), 128.22 (CH, s), 128.27 (CH, s), 128.30 (CH, d, $J = 6.1$ Hz), 128.40 (CH, s), 128.92 (CH, s), 132.54 (CH, d, $J = 18.3$ Hz), 133.05 (CH, d, $J = 19$ Hz), 133.14 (CH, d, $J = 19.1$ Hz), 134.22 (CH, d, $J = 20.5$ Hz), 136.84 (C, d, $J = 9.9$ Hz), 138.51 (C, d, $J = 9.9$ Hz), 138.83 (C, d, $J = 9.9$ Hz), 139.36 (C, d, $J = 8.9$ Hz) ppm. ^{31}P NMR: δ −16.87 (s), −20.00 (br.s) ppm. MS (240°C): m/z (relative %): 611 M + (100), 595 (21), 533 (3), 517 (3), 486 (1), 454 (6), 425 (12), 409 (21).

*4.6. Hydrocarbons **10a**, **10c** and **10d** (general procedure)*

$AlCl_3$ and $LiAlH_4$ were added to a solution of alcohol **9** in diethyl ether–benzene. After stirring and heating the mixture as stated below, the reaction was quenched with an excess of water, the organic layer was separated and the aqueous layer was extracted with 3 × 10 ml of methylenechloride. The combined extracts were dried with $MgSO_4$ and chromatographed on silicagel with petroleum ether : chloroform (50 : 50).

*4.6.1. (±)-2,2′-Bis(diphenylphosphino)-1,1′-(propane-1,3-diyl)ferrocene (**10a**)*

52 mg (0.085 mmol) of **9a** 2 ml of ether, 2 ml of benzene, 210 mg (1.57 mmol) of $AlCl_3$, 50 mg (1.3 mmol) of $LiAlH_4$ for 100 h at room temperature yielded 24 mg (47%) of **10a**; oil; ^{1}H NMR: δ 1.75 (3H, m), 1.88 (2H, m), 2.36 (1H, m), 3.80 (2H, m), 4.10 (2H, br.s), 4.14 (2H, t, $J = 2$ Hz), 7.00 (4H, t, $J = 7.4$ Hz), 7.11 (2H, t, $J = 7.4$ Hz), 7.17 (6H, m), 7.26 (8H, m) ppm. ^{13}C NMR: δ 23.50 (CH_2, t, $J = 3.5$ Hz), 34.29 (CH_2, t, $J = 3$ Hz), 68.47 (CH, s), 71.43 (CH, s), 71.90 (CH, s), 81.07 (C, t, $J = 5$ Hz), 89.09 (C, t, $J = 8$ Hz), 127.77 (CH, t, J = 3.5 Hz), 128.07 (CH, s), 128.11 (CH, t, J = 3.8 Hz), 128.19 (CH, s), 133.45 (CH, t, J = 10.6 Hz), 134.57 (CH, t, $J = 10.5$ Hz), 137.89 (C, t, $J = 7$ Hz), 139.69 (C, t, $J = 6.7$ Hz) ppm. ^{31}P NMR: δ −25.92 (s) ppm. MS (220°C): m/z (relative %) 594 M + (80), 517 (44), 409 (44).

*4.6.2. (±)-2,4′-Bis(diphenylphosphino)-1,1′-(propane-1,3-diyl)ferrocene (**10c**)*

55 mg (0.09 mmol) of **9c**, 2 ml of ether, 2 ml of benzene, 124 mg (0.93 mmol) of $AlCl_3$, 92 mg (2.4

mmol) of $LiAlH_4$ was heated under reflux for 8 h to yield 12 mg (22%) of **10c**; oil. ^1H NMR: δ 1.90 (2H, m), 2.07 (3H, m), 2.37 (1H, m), 3.36 (1H, s), 3.66 (1H, s), 3.98 (1H, s), 4.12 (1H, s), 4.15 (1H, s), 4.38 (1H, s), 7.15–7.37 (20H, m) ppm. ^{13}C NMR: δ 22.77 (CH_2, d, $J = 6.9$ Hz), 24.20 (CH_2, s), 34.85 (CH_2, d, $J = 4.5$ Hz), 73.02, 73.05, 73.08 (2 × CH), 73.28 (CH, d, $J =$ 2.9 Hz), 73.61 (CH, d, $J = 13$ Hz), 73.89 (CH, d, $J = 17.6$ Hz), ≈ 76.4 (2 × C, m?), 78.05. (CH, dd, $J = 6.4$, 2.6 Hz), 89.35 (C, d, $J = 4.5$ Hz), 90.72 (C, d, $J = 21.9$ Hz), 127.85 (CH, d, $J = 6.9$ Hz), 128.00 (CH, d, $J = 7.7$ Hz), 128.06 (CH, s), 128.09 (CH, d, $J = 6.1$ Hz), 128.21 (CH, d, $J = 6.1$ Hz), 128.24 (CH, s), 128.45 (CH, s), 128.75 (CH, s), 132.42 (CH, d, $J = 18.3$ Hz), 133.04 (CH, d, $J = 18.3$ Hz), 133.34 (CH, d, $J = 19.1$ Hz), 134.10 (CH, d, $J = 19.8$ Hz), 136.87 (C, d, $J = 9.1$ Hz), 138.76–139.01 (3 × C, m?) ppm. ^{31}P NMR: δ −15.84 (br.s), −21.19 (s) ppm. MS (160°C): m/z (relative %) 594 M + (100), 517 (15), 409 (23), 332 (21).

4.6.3. (±)-2,5′-Bis(diphenylphosphino)-1,1′-(propane-1,3-diyl)ferrocene (10d)

70 mg (0.11 mmol) of **9d**, 4 ml of ether, 6 ml of benzene, 108 mg (0.8 mmol) of $AlCl_3$, 48 mg (1.2 mmol) of $LiAlH_4$ for 4 h, at 80°C yielded 21 mg (31%) of **10d**; oil, ^1H NMR: δ 2.00 (2H, br.m), 2.09 (2H, br.m), 2.36 (2H, br. m), 3.30 (2H, m), 3.75 (2H, t, $J = 2$ Hz), 4.37 (2H, d, $J = 1.5$ Hz), 7.11–7.26 (16H, m), 7.26–7.35 (4H, m) ppm. ^{13}C NMR: δ 23.03 (CH_2, d, $J = 6.8$ Hz), 34.85 (CH_2, t, $J = 4.9$ Hz), 69.92 (CH, s), 72.41 (CH, d, $J = 3.8$ Hz), 76.63 (C, d, $J = 6.1$ Hz). 77.84 (CH, dd, J = 7.6, 3.8 Hz). 91.26 (C, d, $J = 21.4$ Hz), 128.00 (CH, s), 128.04 (CH, d, $J = 6.8$ Hz), 128.22 (CH, d, $J = 6.1$ Hz), 128.84 (CH, s), 132.37 (CH, d, $J = 18.3$ Hz), 134.44 (CH, d, $J = 19.8$ Hz), 137.19 (C, d, $J = 9.9$ Hz), 139.11 (C, d, 10.7 Hz) ppm. ^{31}P NMR: δ −21.11 (s) ppm. MS (250°C): m/z (relative %): 596 (84), 595 M + (100), 517 (14), 410 (21), 409 (67), 332 (31), 331 (18).

4.7. Crystal structure analyses [16]

4.7.1. (±)-7a

Crystals of orange–red color were grown by slow evaporation from $CHCl_3$. A specimen of size 0.3 × 0.3 × 0.3 mm was used for diffraction experiments, which were performed at 84(2) K on a modified STOE diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). Unit-cell parameters were obtained by least-squares refinement against the setting angles of 23 reflections ($3° \leqslant \theta \leqslant 11°$). Crystals are monoclinic, of space group $P2_1/c$, with four molecules ($C_{39}H_{37}FeNP_2$; formula weight, 637.5) per unit cell: $a = 18.770(4)$ Å, $b =$ 13.763(3) Å and $c = 12.443(2)$ Å; $\beta = 101.98(3)°$; $V =$ 3144.4(11) Å^3; $d_c = 1.347$ g cm^{-3} (calculated from the cell constants observed at 84(2) K); $F(000) = 1336$.

Intensity data (ω scan; $\Delta\omega = 1.5°$) were collected for two octants of reciprocal space ($0 \leqslant h \leqslant 22$; $-16 \leqslant k \leqslant 0$; $-15 \leqslant l \leqslant 14$, $3° \leqslant \theta \leqslant 26°$), yielding 5526 symmetry independent reflections, of which 3769 are significant ($I > 2\sigma(I)$). Lorentz–polarization correction and an empirical absorption correction (program DIFABS [17]) were applied to the data (μ(Mo Kα) = 0.611 mm^{-1}; ratio of minimum to maximum transmission, 0.699). The structure was solved with direct methods and refined with least squares, using a full-matrix least-squares program (SHELXL93 [17]) which minimizes the quantity $\Sigma\omega(F_o^2 - F_c^2)^2$ with $\omega = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (\max(F_o^2, 0) + 2F_c^2)/3$, $a = 0.05$, b = 21, using all reflections. Anisotropic atomic displacement parameters (ADPs) were refined for all non-hydrogen atoms; H atoms were included at calculated positions ("riding"), an isotropic ADP, was refined for each H atom.

Refinement of 425 parameters against 5517 intensity data and 150 restraints converged at the following values for the reliability indices: $\omega R_2 = [\Sigma[\omega(F_o^2 - F_c^2)^2]/\Sigma[\omega(F_o^2)^2]]^{1/2} = 0.1477$ (for all 5526 reflections), $R_1 = \Sigma \| F_o| - |F_c\| / \Sigma |F_o| = 0.0466$ for 3769 significant reflections and 0.0941 for all 5526 data, Goodness of fit $S = [\Sigma[\omega[F_o^2 - F_c^2)^2]/(n-p)^{1/2} =$ 0.852 (number n of observations, 5517, number p of parameters, 425). Features up to 0.352 electrons Å^{-3} and down to −0.297 electrons Å^{-3} were observed in a final difference electron density map.

Atomic coordinates and equivalent isotropic displacement parameters are given in table 2.

4.7.2. (±)-7c.

Conditions and procedures analogous to the structure determination of **7a**, except where noted explicitly; yellow crystals were grown from CH_2Cl_2–methanol; crystal size, 0.4 × 0.4 × 0.4 mm; temperature, 86(2) K. Unit-cell parameters from 24 reflections with $4° \leqslant \theta \leqslant 10°$. Crystals are triclinic, of space group $P1$, two molecules ($C_{39}H_{37}FeNP_2$; formula weight, 637.5) per unit cell: $a = 9.958(2)$ Å, $b = 10.899(2)$ Å and $c =$ 16.150(3) Å; $\alpha = 72.49(3)°$, $\beta = 78.80(3)°$ and $\gamma =$ 76.21(3)°; $V = 1609.1(5)$ Å^3; $d_c = 1.316$ g cm^{-3} (at 86(2) K); $F(000) = 668$.

Intensity data ($\Delta\omega = 1.0°$) were collected for four octants ($-11 \leqslant h \leqslant 11$, $-12 \leqslant k \leqslant 12$, $-1 \leqslant l \leqslant 19$; $3° \leqslant \theta \leqslant 25°$); 5663 symmetry-independent and 4898 significant reflections. DIFABS [17] absorbtion correction with μ(Mo Kα) = 0.597 mm^{-1}. Refinement (425 parameters; 5655 observations; 150 restraints) converged at $\omega R_2 = 0.1160$ (all 5663 reflections), $R_1 = 0.0413$ (4898 significant reflections), $R_1 = 0.0503$ (all 5663 data), $S = 1.062$ ($n = 5655$; $p = 425$). Maximum and minimum residual electron density: 0.451 electrons Å^{-3}

and down to −0.411 electrons Å^{-3}. Atomic coordinates are given in Table 3.

4.7.3. (±)-7d

Orange crystals were grown from $CHCl_3$; crystal size, 0.5 × 0.4 × 0.2 mm; temperature, 87(2) K. Unit-cell parameters from 34 reflections with $4° \leqslant \theta \leqslant 11°$. Crystals are triclinic, of space group $P1$, two molecules ($C_{39}H_{37}FeNP_2$; formula weight, 637.5) per unit cell: $a = 8.785(9)$ Å, $b = 13.297(10)$ Å, and $c = 14.134(9)$ Å; $\alpha = 74.33(6)°$, $\beta = 85.74(7)°$ and $\gamma = 75.74(6)°$, $V = 1540.7(22)$ Å^3, $d_c = 1.374$ g cm^{-3} (at 87(2) K); $F(000) = 668$.

Intensity data ($\Delta\omega = 1.0°$) were collected for four octants ($-10 \leqslant h \leqslant 10$, $-14 \leqslant k \leqslant 15$, $0 \leqslant l \leqslant 16$, $3° \leqslant \theta \leqslant 25°$); 5420 symmetry independent and 4644 significant reflections. DIFABS [17] absorbtion correction with μ(Mo Kα) = 0.623 mm^{-1}. Refinement (426 parameters; 5414 observations; 150 restraints) converged at $\omega R_2 = 0.1009$ (all 5420 reflections), $R_1 = 0.0373$ (4644 significant reflections with $F_o > 4\sigma(F_o)$), $R_1 = 0.0486$ (all 5420 data), $S = 1.078$ ($n = 5414$; $p = 426$). Maximum and minimum residual electron density: 0.351 electrons Å^{-3} and down to −0.394 electrons Å^{-3}. Atomic coordinates are given in Table 4.

Acknowledgments

Thanks are due to B. Jedlicka for assistance in performing the crystal structure determination of **7a** and to the Fonds zur Förderung der wissenschaftlichen Forschung (P-CHE8414 and P-CHE9859) for financial support.

References and notes

[1] (a) T. Hayashi, K. Yamamoto and M. Kumada, *Tetrahedron Lett.*, (1974) 4405; (b) T. Hayashi, M. Tajika, K. Tamao and M. Kumada, *J. Am. Chem. Soc., 98* (1976) 3718.
[2] For an actual exhaustive compilation of ferrocene-based asymmetric catalysts refer to: H. Brunner and W. Zettelmeier, *Handbook of Enantioselective Catalysis with Transition Metal Compounds*, VCH, Weinheim, 1993; A. Togni and T. Hayashi (eds.), *Ferrocenes*, VCH, Weinheim, 1995.
[3] There are only a few exceptions of chiral ferrocenyl-phosphino ligands not being derived from the C_1-symmetrical base structure **1**: cf.: T. Hayshi, A. Yamamoto, M. Hojo and Y. Ito, *J. Chem. Soc., Chem. Commun.*, (1989) 495; N. Deus, D. Robles and R. Herrmann, *J. Organomet. Chem., 386* (1990) 253; M. Sawamura, A. Yamauchi, T. Takegawa and Y. Ito, *J. Chem. Soc., Chem. Commun.*, (1991) 874.
[4] D. Marquarding, H. Klusacek, G. Gokel, P. Hoffmann and I. Ugi, *J. Am. Chem. Soc., 92* (1970) 5389.
[5] Cf.: J. Halpern, in J.D. Mosher (ed.), *Asymmetric Synthesis*, Vol. 5, Academic Press, New York, 1985, pp. 41–69; K.E. Koenig, in J.D. Mosher (ed.), *Asymmetric Synthesis*, Vol. 5, Academic Press, New York, pp. 71–101.
[6] B. Jedlicka, C. Kratky, W. Weissensteiner and M. Widhalm, *J. Chem. Soc., Chem. Commun.*, (1993) 1329.
[7] A. Mernyi, C. Kratky, M. Widhalm and W. Weissensteiner, *J. Organomet. Chem.*, (1995).
[8] S. Hinterberger, unpublished, 1993.
[9] G. Kutschera, unpublished, 1993.
[10] For clarity, we have chosen a labeling scheme for the atoms of the cyclopentadiene rings which is not in accord with IUPAC rules. The stereochemical descriptors for the metallocene chirality, S or R, are indexed m1 or m2 if related to the upper or lower ring respectively. The viewing direction and the sequence of substituents with decreasing priority according to the CIP system is exemplified for 2,2′-bis(diphenylphosphino)-1,1′-(1-dimethylaminopropane-1,3-diyl) ferrocene (**7a**) which was derived from (S)-**5**. Compare with figure in section 2.
[11] This behavior can be rationalized if viewing **7a** and **11** as C_s-symmetrical diphosphinoferrocenes with a (small) chiral interference from the asymmetric α-carbon. The relationship between the two isomers resembles that between epimers, since the structural differences arise from the α-C with a proximal P–N arrangement in **7a** and distal P–N arrangement in **11**. Thus the observed small and reversed CD effects qualitatively agree with intuitive expectations.
[12] PCMODEL, *Molecular Modeling Software*, Serena Software, Bloomington, IN, 1992.
[13] I.R. Butler, W.R. Cullen, J. Reglinsky and S.J. Rettig, *J. Organomet. Chem., 249* (1983) 183.
[14] M. Rosenblum, A.K. Banerjee, N. Danieli, R.W. Fish and V. Schlatter, *J. Am. Chem. Soc., 85* (1963) 316; P. Dixneuf and R. Dabard, *Bull. Soc. Chim. Fr., 7* (1972) 2847.
[15] G. Tainturier, K. Chhor y Sok and B. Gautheron, *C.R. Acad. Sci., Sèr. C, 277* (1973) 1269.
[16] Supplementary data (bond length, bond angles, torsional angles and structure factors) have been deposited at the Cambridge Crystallographic Data Centre.
[17] The following computer programs were used for the crystallographic work: *SHELXTL PC, Version 4.1*, Siemens Analytical Instruments, Inc., Madison, WI, 1990; *SHELXL-93, a Program for the Refinement of Crystal Structures from Diffraction Data*, G.M. Sheldrick, University of Göttingen, Göttingen 1993; DIFABS, N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 158.