Enantioselective Catalysis 113:[1] New Menthylphosphane Ligands Differing in Steric and Electronic Properties

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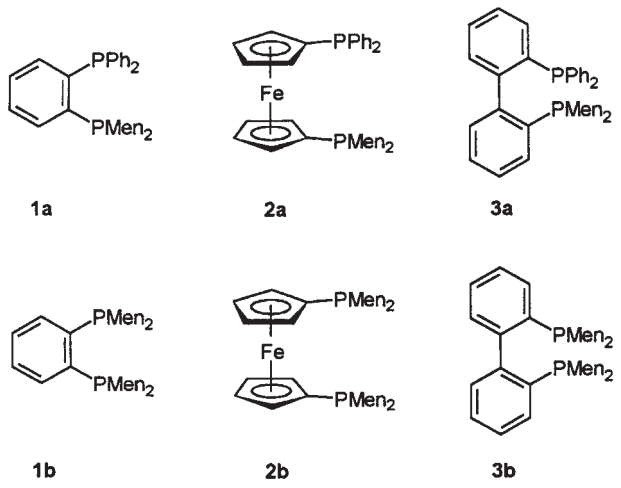
A concept for bisphosphane ligands was developed, in which chirality is derived from the optically active (1*R*,3*R*,4*S*)-menthyl substituents in $PMen_2$ groups and the backbone between the phosphorus units is varied (o-phenylene, 2,2′-biphenylene, 1,1′-ferrocenediyl); one of the two $PMen_2$ groups was also replaced by a PPh_2 unit. The synthesis and characterisation of seven new menthylphosphanes is described. Emphasis is put on the NMR assignment of the menthyl protons by two-dimensional methods and ^{13}C–^{1}H shift correlation. The ligands have been used in Rh and Ni complexes in several model reactions of enantioselective catalysis giving optical inductions in the low to middle range.

Introduction

Menthyl derivatives play a prominent role in the synthesis of optically active compounds. In particular, in the early days of catalytic asymmetric C–C bond formation, the highest optical yields were obtained using phosphanes with menthyl substituents.[2] Meanwhile dozens of menthylphosphanes have been synthesised and used in different transition-metal-catalysed asymmetric homogeneous,[3] heterogeneous[4] and two-phase reactions.[5] Menthyl-substituted phosphanes have been used for studying the epimerisation and halogen exchange at the phosphorus atom[6] and have been the object of extensive NMR investigations.[7] The menthyl unit is also used for stabilising diphosphenes,[8] for the synthesis of chiral 1,1-diphosphanes, phosphiranes and phosphetanes[9] and it is part of a chirally modified zirconocene catalyst used successfully in asymmetric carbomagnesiation of unactivated alkenes.[10]

Most of the optically active chelate phosphanes, such as diop,[11] prophos,[12] bppfa,[13] biphemp,[14] binap,[15] or norphos,[16] involve a chiral skeleton bearing two diphenylphosphanyl groups. The chiral information is transferred from the ligand to the catalytically active metal center via the arrangement of the phenyl rings of the diphenylphosphanyl groups. Our intention was to develop a series of easily accessible optically active chelate phosphanes, having the menthyl chirality next to the phosphorus atoms.

In the chelating menthylphosphanes the isopropyl group of the menthyl unit is close to the phosphorus atom. Hence there should be a direct interaction with the pocket of the catalyst, in which the enantioselective reaction takes place. The backbone between the two dimenthylphosphorus units was varied (*o*-phenylene, 2,2′-biphenylene, 1,1′-ferrocenediyl). One dimenthylphosphanyl group was replaced by a diphenylphosphanyl group to change the steric and electronic properties of the ligands. A correlation between the structure of the ligands and their reactivity and selectivity in asymmetric catalysis is expected.[17]



Scheme 1

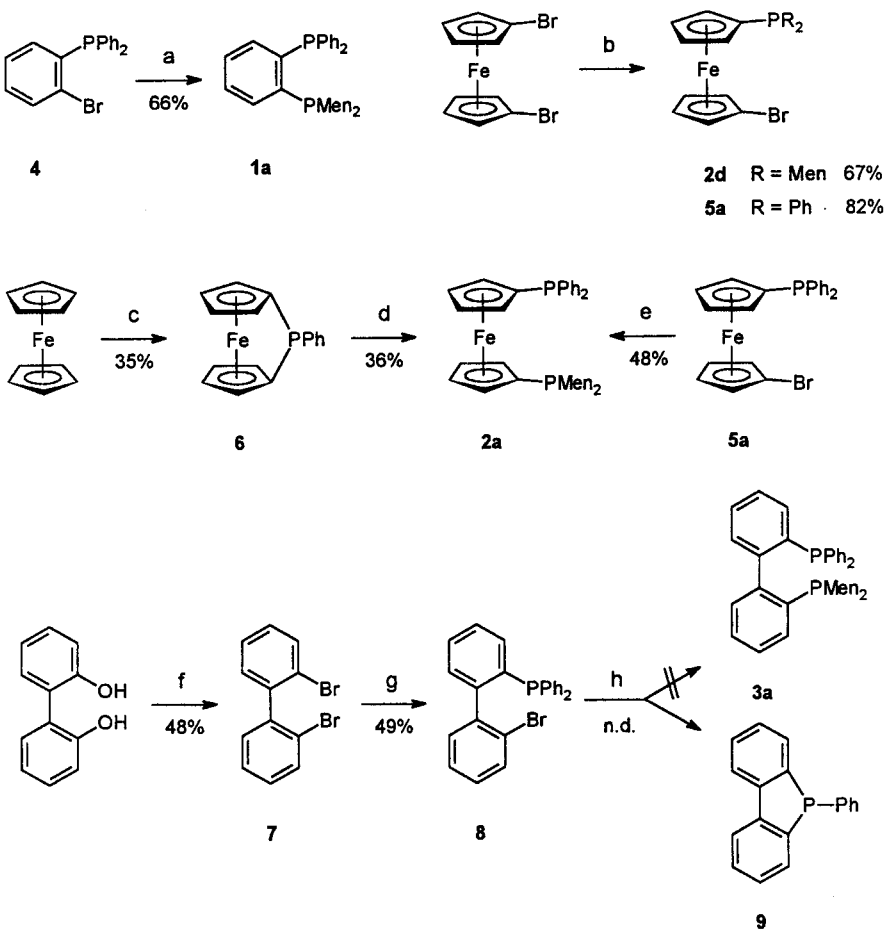
Synthetic Strategy

For the preparation of the menthylphosphanes the following strategy was chosen. To introduce the dimenthylphosphanyl unit, (–)-chlorodimenthylphosphane[18] was used. It was prepared from the Grignard derivative of (–)-menthyl chloride[19] and PCl_3. Starting from dihaloarene compounds the tetramenthylbisphosphanes should be accessible by quenching the appropriate organometallic derivative with two equivalents of the chlorodimenthylphosphane. Using this strategy, only one side product, the corresponding monosubstituted dimenthylphosphanyl arene, is eventually obtained. The purification of the products should occur by flash chromatography or recrystallisation. For the preparation of the mixed dimenthylphosphanyl-diphenylphosphanyl ligands a successive substitution of the bromo substituents of a dibromoarene compound was considered.

Dimenthylphosphanyl-diphenylphosphanylarenes

The precursor for the mixed bisphosphanebenzene **1a** was (2-bromophenyl)diphenylphosphane **4**. It was synthesised by Pd-catalysed coupling of diphenyl(trimethylsilyl)phosphane and bromoiodobenzene according to a procedure discovered by Stille.[20] Bromoiodobenzene was prepared from 2-bromoaniline via a Sandmeyer reaction.[21] Compound **4** was treated with butyllithium at –70°C and quenched with $ClPMen_2$ to give **1a** in 66% yield after chromatography on silica gel (Scheme 2).

For the preparation of the ferrocenyl- and biphenyl-bridged dimenthylphosphanyl-diphenylphosphanyl ligands a successive substitution of the bromo substituents of the corresponding dibromoarene was performed. For dibromoferrocene the procedure developed by Lai and



Scheme 2

(a) 1. BuLi, THF, –70°C, 2. $ClPMen_2$, Et_2O, –30°C → reflux; (b) 1. BuLi, THF, –50°C, 2. **5a:** $ClPPh_2$, THF, –40°C → r.t.; **2d:** $ClPMen_2$, THF, –40°C → reflux; (c) 1. BuLi, hexane, TMEDA, r.t., 85%. 2. $PhPCl_2$, hexane, –70°C → r.t., 41%; (d) 1. PhLi, Et_2O, r.t., 2. $ClPMen_2$, THF, –50°C → reflux; (e) 1. t-BuLi, Et_2O, –78°C, 2. $ClPMen_2$, THF, –70°C → reflux; (f) 1. PPh_3Br_2, MeCN, 60°C, 2. 280°C; (g) 1. BuLi, THF, –75°C, 2. $ClPPh_2$, Et_2O, –70°C → r.t.; (h) 1. BuLi, THF, –75°C, 2. $ClPMen_2$, THF, –75°C → r.t.

Dong was chosen[22] which could be extended to the biphenyl system. Up to now, the required 2,2′-dibromo-1,1′-biphenyl **7** was prepared starting from expensive materials[23] or in multistep reactions,[24, 25] e.g. from 1-iodo-2-nitrobenzene, by an Ullmann coupling followed by a catalytic reduction of the nitro to the amino groups and a Sandmeyer reaction to transform the amino to the bromo functions.[24] Here a new one-pot synthesis starting from inexpensive 2,2′-dihydroxy-1,1′-biphenyl is presented. It is a modified procedure used by Takaya et al. to prepare the binap precursor 2,2′-dibromo-1,1′-binaphthyl.[26] On a 0.2 mol scale colourless crystals of **7** were obtained in 48% yield after chromatography and recrystallisation from methanol.

The monolithiation of 1,1′-dibromoferrocene and 2,2′-dibromo-1,1′-biphenyl **7** proceeded smoothly at low temperature (–70 to –40°C) in THF to give 1-bromo-1′-lithioferrocene and 2-bromo-2′-lithio-1,1′-biphenyl, respectively, which were quenched with $ClPPh_2$ and $ClPMen_2$ to give the bromo-phosphanyl derivatives **2d** (67%), **5a**[27] (83%) and **8** (49%), respectively, after purification by chromatography on silica gel or alumina (Scheme 2). The subsequent lithiation of compound **5a** required *tert*-butyllithium to give 1-lithio-1′-diphenylphosphanylferrocene, which was reacted with chlorodimenthylphosphane to give 1-dimenthylphosphanyl-1′-diphenylphosphanylferrocene **2a** in 48% yield after chromatography on silica gel. Alternatively, **2a** could be synthesised by using a ring-opening reaction of (1,1′-ferrocenediyl)phenylphosphane **6**[28] with phenyllithium performed by Seyferth and Withers.[29] The intermediate 1-lithio-1′-diphenylphosphanylferrocene was treated as described above to give **2a.** In addition, the iodo analogue of **5a** was synthesised by Pd-catalysed coupling of one equivalent of diphenyl(trimethylsilyl)phosphane and 1,1′-diiodoferrocene (see also preparation of **1a**). As expected, the two iodo-substituted cyclopentadienyl rings reacted independently in the coupling reaction. Hence the product distribution is close to the ideal case of 1:2:1 for recovered starting material, the desired 1-iodo-1′-diphenylphosphanylferrocene (**5b**) and the bissubstituted bis(diphenylphosphanyl)ferrocene. The synthetically useful ferrocenyl derivative **5b** has been isolated so far only as a byproduct.[29b]

As biphenyl-based bisphosphanes are an important class of chiral ligands, the systematic synthesis of menthylphosphanes was extended to the 1,1′-biphenyl backbone.

In particular, the atropisomeric bisphosphanes of the biphemp[14]/bichep[30] ligand family served as model compounds. Though much effort has been made on the preparation and variation of these axially dissymmetric ligands,[31] the synthesis still requires many steps and a resolution procedure. With the chirality in the menthyl substituents, a resolution step is not necessary.

Compound **8** was treated with one equivalent of butyllithium in THF at –75 °C to perform a halogen–metal exchange. After stirring at this temperature for 30 minutes, the 2-lithio-2′-diphenylphosphanyl-1,1′-biphenyl was quenched with $ClPMen_2$. Surprisingly, not the expected bisphosphane **3a**, but the *P*-phenyl-dibenzophosphole **9** was isolated after chromatography on silica gel using a petroleum ether/Et_2O gradient (Scheme 2). Also **9** was isolated, when other electrophiles such as DMF or CO_2 were added to 2-lithio-2′-diphenylphosphanyl-1,1′-biphenyl or when the Grignard compound was used instead of the lithio species. Recently Schlosser et al. published their results and mechanistic studies concerning the unsuccessful attempts to prepare Uehara's **bpbp.**[32] They showed, that the product of quenching 2,2′-dilithiobiphenyl with chlorodiphenylphosphane is not **bpbp**, but a 1:1 mixture of 5-phenyl-*5H*-dibenzophosphole (**9**) and triphenylphosphane. Obviously, the monolithio-monophosphane formed in the first step of the reaction of 2,2′-dilithiobiphenyl with $ClPPh_2$ or by halogen–metal exchange of **8** with one equivalent of butyllithium underwent an intramolecular ring closure, affording the cyclic phosphane **9** and phenyllithium which eventually reacted with $ClPPh_2$ or $ClPMen_2$, respectively. However, the reaction of $ClPPh_2$ with 2,2′-dilithio-6,6′-dimethylbiphenyl or 2,2′-dilithio-1,1′-binaphthyl smoothly proceeded to form the bisphosphanes biphemp[14]or binap,[33] respectively. Hence, special steric and electronic requirements seem to be necessary for the observed ring closure. Schlosser et al. tentatively postulated a concertedness for the substitution at the phosphorus atom (Figure 1 right).[32]

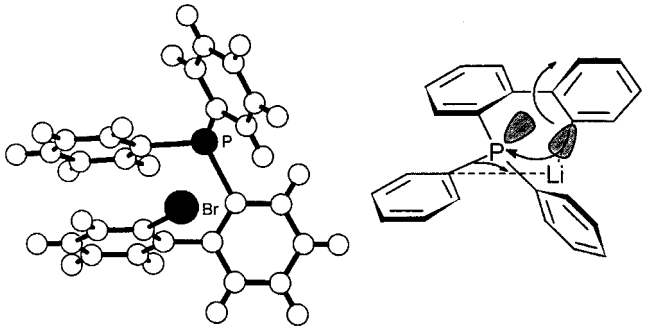
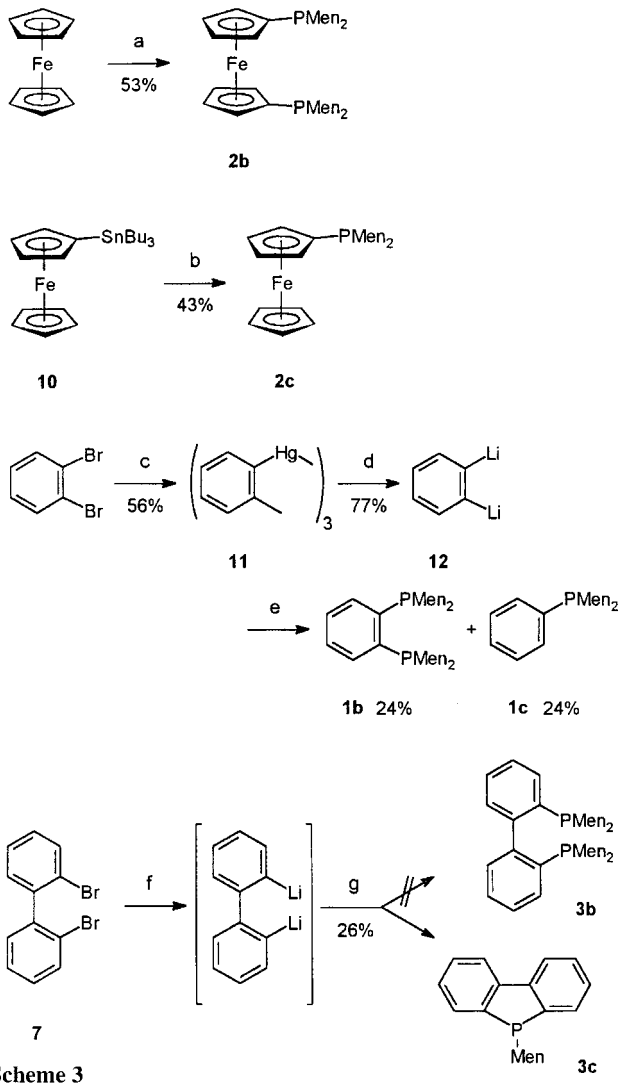


Figure 1

A skew geometry showing an antiparallel orientation of the organometallic bond with respect to the phosphorus lone pair explains the observed reaction mode. The collinear attack which is characteristic for nucleophilic substitution at carbon centers is replaced by a winding-in motion that couples the shortening of the distance between phosphorus and the metal-bearing *ortho*-carbon atom to a rotation around the central biphenyl axis. A similar geometry which is consistent with Schlosser's results was calculated for the precursor **8** with the molecular modeling program sybil2 (Figure 1 left).[34] In the calculated structure one phenyl ring of the diphenylphosphanyl unit is adjusted parallel to the bromo-substitutued biphenyl moiety. This geometry should also be favourable for the above discussed reaction mode. Thus, it is not possible to prepare 2-dimenthylphosphanyl-2′-diphenylphosphanyl-1,1-biphenyl (**3a**) by reaction of **8** with butyllithium and $ClPMen_2$.

Bis(dimenthylphosphanyl)arenes

Only very few general and efficient homogeneous catalytic methods are known for the reduction of aldehydes and ketones.[35] One example is the achiral cationic rhodium(I) catalyst with 1,1′-bis(diisopropylphosphanyl)ferrocene, which hydrogenates a broad range of aldehydes and ketones under mild conditions,[36] the important factors for catalytic efficiency being backbone flexibility and electron-rich (di- or trialkyl-substituted) phosphorus atoms. To combine these requirements with chirality, the isopro-



Scheme 3

(a) 1. BuLi, hexane, TMEDA, r.t., 85%, 2. $ClPMen_2$, THF, –78°C → reflux, 62%; (b) 1. BuLi, THF, –78°C, 2. $ClPMen_2$, THF, –70°C → reflux; (c) Na/Hg, Et_2O, r.t.; (d) Li, Et_2O, r.t.; (e) $ClPMen_2$, Et_2O, –60°C → r.t.; (f) BuLi, Et_2O, 0°C; (g) $ClPMen_2$, THF, –l5 °C → r.t.

pyl units in 1,1′-bis(diisopropylphosphanyl)ferrocene were exchanged by the optically active menthyl units (Scheme 3).

1,1′-Bis(dimenthylphosphanyl)ferrocene **2b** was thought to be accessible from the known 1,1′-dilithioferrocene–TMEDA adduct[37] and chlorodimenthylphosphane. In the first attempts a 1:1 mixture of the mono- and disubstituted ferrocenes resulted (determined by ^{31}P NMR integration) not separable by chromatography or recrystallisation. The two singlets in the ^{31}P NMR at δ–23.3 and –24.1 could not be assigned. After prolonged refluxing of dilithioferrocene–TMEDA adduct with 2.2 equivalents of $ClPMen_2$ in a THF/petroleum ether 80:110 solvent mixture, pure **2b** (δ–24.1) was obtained.

For the synthesis of the monosubstituted dimenthylphosphanylferrocene **2c** the procedure published by Kagan was applied. Tributylstannylferrocene **10** was treated with butyllithium to generate the pure monolithiumferrocene,[38] which was quenched with $ClPMen_2$ to give **2c** in reasonable yields after chromatography on alumina and recrystallisation from pentane.

For preparing the 1,2-bis(dimenthylphosphanyl)benzene (**1b**), the starting material 1,2-dilithiobenzene (**12**) was obtained through transmetallation from *o*-phenylenemercury (**11**).[39] After quenching with $ClPMen_2$ and workup the side-product tetramenthylbisphosphane could be isolated and characterised by spectroscopic means. The second side-product, the monosubstituted dimenthylphosphanylbenzene **1c** could not be separated from **1b** by chromatography or recrystallisation. Thus, a 1:1 mixture (^{31}P NMR integration) of **1b** and **1c** was obtained and used as such. The reason for the formation of **1c** may be partial hydrolysis during the preparation of **12**.

The synthesis of the biphenyl-bridged tetramenthylbisphosphane **3b** was thought to be analogous to the preparation of one of the first axial chiral bisphosphanes, Uehara's 2,2′-bis(diphenylphosphanyl)-1,1′-biphenyl **bpbp.**[24] Starting from a solution of 2,2′-dibromo-1,1′-biphenyl **7** in anhydrous diethyl ether, 2.2 equivalents of butyllithium were added to form the corresponding 2,2′-dilithio-1,1′-biphenyl, which precipitated. When a solution of chlorodimenthylphosphane in THF was added, after workup not the expected 2,2′-bis(dimenthylphosphanyl)-1,1-biphenyl **3b** but the 5-menthyl-*5H*-dibenzophosphole (**3c**) was isolated in 26% yield. The same product was obtained, when $ClPMen_2$ was added at –78 °C and the solution was refluxed for 15 hours. This result is consistent with our observations described above and those made by Schleyer, who also obtained a dibenzophosphole derivative after quenching the 2,2′-dilithiobiphenyl with chlorotrimethylstannane.[40] Following this sequence, it was not possible to prepare 2,2′-bis(dimenthylphosphanyl)-1,1-biphenyl (**3b**).

NMR Spectra

All the new compounds were characterised by NMR and mass spectroscopy and elemental analysis. In general, the relative position of the ^{31}P resonances may be taken as a guide to the ligand basicity and the σ-donor property of the phosphane ligand.[27, 41] The *o*-phenylene- and 2,2′-biphenylene-substituted phosphorus nuclei resonate at lower field than the 1,1′-ferrocenediyl-substituted nuclei. The same trend is evident for mono- and bisphosphanes, respectively, although the difference for the ferrocenyl phosphanes **2c** and **2b** is 0.8 ppm, whereas it is 10.0 ppm between **1c** and **1b.** The dimenthyl-substituted phosphane units in turn are observed at higher field than their phenyl analogues which indicates their higher basicity.

Emphasis was put on the complete assignment of the ^{1}H and ^{13}C resonances of the menthyl fragments by means of two-dimensional NMR techniques and reference to the literature,[3a,3g,7,31] e.g. with (–)-dimenthylmethylphosphane.[7a] The menthyl groups in dimenthylphosphanyl-substituted compounds are diastereotopic. Consequently, all menthylphosphanes (except **3c**, the only monomenthylmonophosphane) have 20 non-equivalent carbon atoms (which all are separated, see experimental part) and 26 non-equivalent hydrogen atoms. At a glance, all the ^{1}H NMR spectra of the ligands **3c, 1a** and **2a** shown in Figure 2 seem to be similar. However, only H-8 resonates always at lowest field. The sequence of the other protons depends on the substitution pattern. Especially the signal for the equatorial H-2 shows large chemical shift differences: in **3c** it appears at δ 0.76, in **2a** at δ 2.02 and ca. 1.2. The ferrocenyl-substituted menthylphosphanes **2a–d** exhibit typical patterns in their ^{1}H NMR spectra. Therefore, starting from **2a** it was possible to assign the ^{1}H NMR spectra of the ligands **2b–d** completely.

Catalytic Results

Rhodium complexes, generated in situ from $[Rh(cod)Cl]_2$ and the ligands **1a, 1b, 2a, 2b, 3c**, were used as catalysts in the asymmetric homogeneous hydrogenation of (*Z*)-α-acetamidocinnamic acid,[42] methyl pyruvate, and ketopantolactone[43] and in the hydrosilylation of acetophenone with diphenylsilane.[44] The Grignard cross-coupling of 1-phenylethylmagnesium chloride with vinyl bromide[45] was catalysed with nickel complexes generated in situ.

The results of the asymmetric hydrogenations are summerised in the Table. Methanol is the most favourable solvent in these hydrogenations, though toluene is necessary to increase the solubility of the ligands and to prepare the catalysts. In the hydrogenation of ketopantolactone toluene was used as the standard solvent.[43]

The in situ catalysts exhibited good to high hydrogenation activity, when (*Z*)-α-acetamidocinnamic acid was used as a substrate. Ligand **1a** needed about 20 h to hydrogenate the dehydroamino acid with 23% optical yield. Higher pressure enhanced the hydrogenation rate, the enantiomeric excess remaining unchanged (runs 1 and 2). The most active ligand was **2a**, which completed the reaction under smooth conditions (r.t., 1 bar) within a few hours (run 4). When the molar ratio substrate/Rh was lowered from 50:1 to 100:1 and 200:1 the catalyst activity decreased while the selectivity increased from 12 to 24% ee (*S*) (runs 4–6). With higher pressures the reaction was

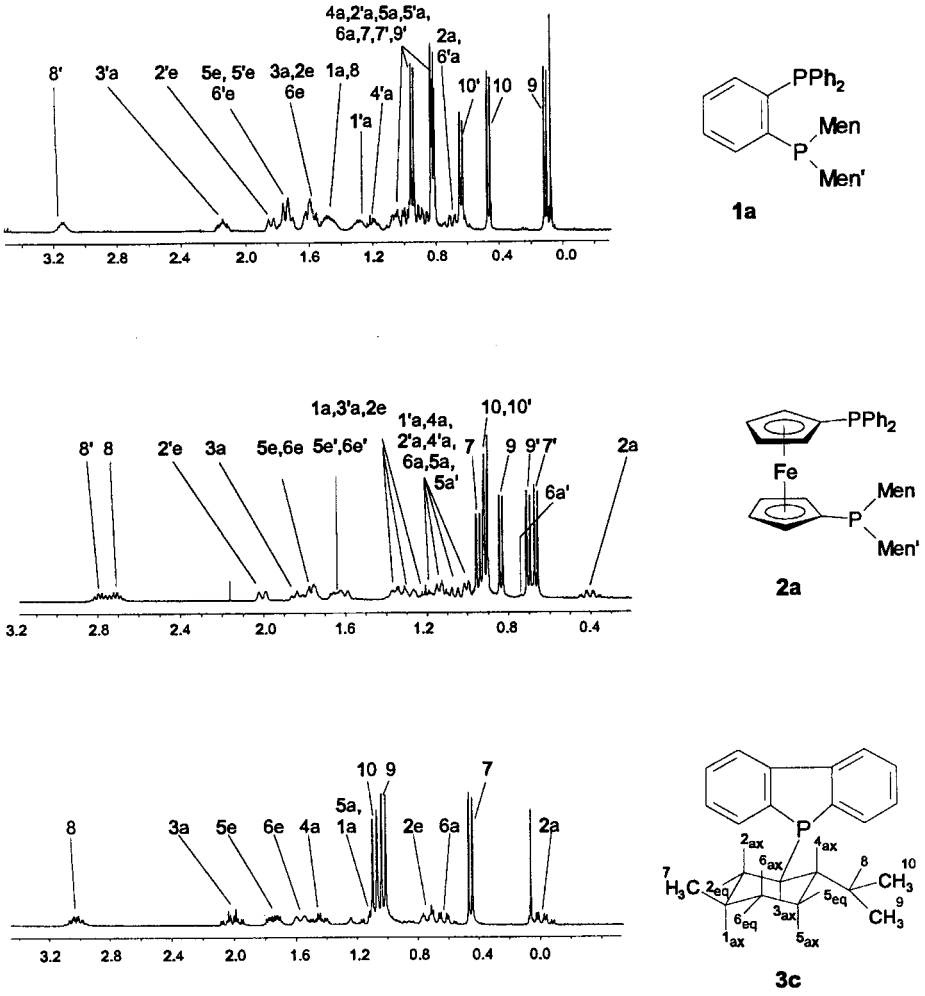


Figure 2

Table. Enantioselective Hydrogenation of Substrate (4 mmol) in Solvent (11 mL) at 25°C

Entry	Substrate[a]	Ligand	Ratio/Rh[b]/Ligand Substrate	Solvent[c]	Pressure (bar)	Time (h)	Yield[d] (%)	*e.e.* (%) (Config.[e])
1	A	**1a**	100:1:1.1	MeOH/toluene	1	20	> 95	23 (*S*)
2	A	**1a**	100:1:1.1	MeOH/toluene	10	3	> 95	24 (*S*)
3	A	**1b**[f,g]	100:1:1.1	MeOH/toluene	10	20	50	9 (*R*)
4	A	**2a**	50:1:1.1	MeOH/toluene	1	3	> 95	12 (*R*)
5	A	**2a**	100:1:1.1	MeOH/toluene	1	12	> 95	22 (*R*)
6	A	**2a**	200:1:1.1	MeOH/toluene	10	17	> 95	24 (*R*)
7	A	**2a**	100:1:1.1	MeOH/toluene	30	1	> 95	25 (*R*)
8	A	**2a**	50:1:1.1	MeOH/toluene	10	1	> 95	18 (*R*)
9	A	**3c**	100:1:2.2	MeOH/toluene	30	3	> 95	22 (*S*)
10[h]	B	**2a**	200:1:1.1	MeOH/toluene	30	19	> 99	11 (*S*)
11[h]	B	**3c**	200:1:1.1	MeOH/toluene	30	20	70	20 (*S*)
12[i]	C	**1a**	100:1:1.1	toluene	50	40	10	9 (*R*)
13[i]	C	**2a**	100:1:1.1	toluene	50	65	> 99	20 (*S*)
14[i]	C	**2b**	100:1:1.1	toluene	50	40	95	12 (*S*)

[a] A = (*Z*)-α-acetamidocinnamic acid; B = methyl pyruvate, C = ketopantolactone.
[b] Prepared *in situ* with $[Rh(cod)Cl]_2$.
[c] MeOH/toluene 10:1 mL or toluene 11 mL.
[d] The yield was checked by ^1H NMR (80 MHz), see also footnotes h and i.
[e] The enantiomeric excess of N-acetylphenylalanine was determined by polarimetry, $[\alpha]_D$ + 46.8 (c = 1.95, EtOH).[50]
[f] The 1:1 mixture of **1b and 1c** was used as the ligand.
[g] Deposition of a small amount of rhodium was observed.
[h] Substrate (8 mmol) was hydrogenated; the chemical yield was determined by ^1H NMR spectroscopy (80 MHz), the opticalyieldby GC (Chirasil-L-Val, 25 m).
[i] Substrate (4 mmol) was hydrogenated at 50°C; the chemical and optical yields were determined by GC.[43]

complete in less than 1 h, but the selectivity diminished (runs 6–8). About 5–10 min after dissolving **2b** and $[Rh(cod)Cl]_2$ in 1 mL of toluene a pink solid precipitated which was catalytically inactive. The in situ catalyst obtained with the 1:1 mixture of **1b** and **1c** exhibited a low hydrogenation activity (run 3). In all hydrogenation reactions using this mixture a deposition of small amounts of rhodium was observed. This is consistent with observations made in other groups, working with this class of ligands.[3g, 31] In general, the observed enantiomeric excesses were lower than the values obtained with the similar ligand 2,3-bis(dimenthylphosphanyl)maleic anhydride, which produced up to 70% ee with (*Z*)-α-acetamidocinnamic acid.[3g]

When methyl pyruvate was hydrogenated with Rh catalysts to methyl lactate only **2a** and **3c** showed catalytic activity (runs 10 and 11). Ligand **1a** was completely inactive. Similar results were obtained when ketopantolactone was reduced to pantolactone (runs 12–14). With **1a** as a ligand, only 10% conversion was achieved after 40 hours (run 12), whereas **2a** catalysed the reaction completely within 65 hours (run 13). Interestingly, in all cases observed, **1a** and **2a**, both diphenylphosphanyl-dimenthylphosphanyl ligands, differing only in the bridge between the two phosphorus atoms, yielded the products in opposite configuration (compare runs 1, 2 and 4–8, 12 and 13).

In the hydrosilylation of acetophenone with diphenylsilane[44] almost quantitative hydrosilylation and chemical yields (97–99% and 92–97%, respectively) were obtained with **1a, 2a**, and **3c**. Only **1b** and **2b**, both tetramenthyl-substituted bisphosphanes, gave 33% and 38% of silylenol ether, respectively, which on hydrolysis reverts to acetophenone. Obviously, this is a consequence of the bulkiness of the ligands. After hydrolysis, the monophosphane **3c** yielded 24% ee of (*S*)-1-phenylethanol in 97% chemical yield. All the bisphosphanes produced racemic 1-phenylethanol within the limits of error (< 0.5% ee).[17]

In the nickel-catalysed Grignard cross-coupling of 1-phenylethylmagnesium chloride with vinyl bromide[45] to form 3-phenylbut-1-ene, the 1:1 mixture of the bisphosphane **lb** and the monophosphane **1c** gave the highest enantiomeric excess of the menthylphosphanes described here [32% (*S*)], whereas **1a, 2a** and **2b** produced only low ee's.[17]

All manipulations involving phosphanes were performed under exclusion of air using standard Schlenk techniques under purified N_2. If organometallic reagents were involved, H_2O was also excluded. Solvents were dried and degassed according to standard procedures[46] and stored under nitrogen. THF was dried from potassium benzophenone ketyl and freshly distilled before use. H_2O and solvents for chromatography were degassed by bubbling N_2 through the fluids for at least 8 h. Chromatographic materials (silica gel 60, 65–200 μm, Merck), and alumina 90 (neutral, activity II-III, Merck) were saturated with N_2. TLC was performed on Merck silica gel 60 F_{254} plates (visualisation with UV light and $KMnO_4$ solution). Three acronyms will be used successively: Men for the (1*R*,3*R*,4*S*)-menthyl fragment, Fc for ferrocene and PE for petroleum ether (bp 40–60°C).

Melting points were determined using SMP-20 (Büchi) and were not corrected. Vibrational spectra were recorded on a Beckman spectrometer IR 4240 or a Bio-Rad FT-IR FTS 155 in CH_2Cl_2 solution or as KBr pellets. For MS, the MAT 311 A (electron impact deionisation) and the MAT 95 (field desorption) apparatus (both Finnigan) were used. The intensities are relative to the basic peak (I = 100%), possible interpretations are given within brackets. Optical rotations were measured with a Perkin–Elmer model 241 polarimeter on the specified solutions in 1 dm cells at r.t. Elemental analyses were performed by the Mikroanalytisches Labor of the Universität Regensburg. ^{1}H NMR spectra were recorded using the following spectrometers: FT 80 A (80 MHz, Varian), AC 250 (250 MHz, Bruker), ARX 400 (400 MHz, Bruker) and AMX 500 (500 MHz, Bruker). The chemical shifts are given in units of the δ scale relative to internal TMS. The same standard was used for the ^{13}C NMR spectra (including DEPT sequences), performed on AC 250 (63 MHz), ARX 400 (101 MHz), and AMX 500 (125 MHz). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet etc, dd = doublet from doublet. ddd = doublet from doublet from doublet etc., m = multiplet, cm = centered multiplet, b = broad, p = pseudo). coupling constant in Hz, integration and assignment. Peak assignments were possible after two-dimensional experiments (COSY, ECOSY, TOCSY, HMBC and HMQC experiments). For the ^{31}P NMR spectra (^{1}H-decoupled). the ARX 400 (162 MHz), external standard 85% H_3PO_4, was used.
BuLi was purchased from Aldrich and used directly. The compounds (–)-chlorodimenthylphosphane,[18] (–)-menthyl chloride,[19] diphenyl(trimethylsilyl)phosphane,[20] (2-bromophenyl)diphenylphosphane (**4**),[20] 1-bromo-2-iodobenzene,[21] (1,1′-ferrocenediyl)phenylphosphane (**6**),[28] 1,1-dilithioferrocene (TMEDA adduct),[37] diiodoferrocene,[37] dibromoferrocene,[37] tributylstannylferrocene (**10**),[38] 1,2-dilithiobenzene (**12**),[39] *o*-phenylenemercury (**11**)[47] and bis(acetonitrile)palladium chloride $(MeCN)_2PdCl_2$[48] were prepared according to literature methods.

Preparation of 1′-Substituted 1-Bromoferrocenes and 2′-Substituted 2-Bromobiphenyls; General Procedure:
To a cooled (–50°C) 0.2 M solution of dibromoferrocene or 2,2′-dibromo-1,1′-biphenyl in freshly distilled THF was added dropwise 1.6 M BuLi in hexane (1.05 equiv). The resulting solution was stirred at this temperature for about 30 min, during which time1-bromo-1′-lithioferrocene gradually precipitated (2-bromo-2′-lithio-1,1′-biphenyl did not precipitate). Then a 1 M solution of the chlorophosphane $ClPR_2$ (1.1 equiv) in THF was added slowly and the reaction mixture was allowed to warm up to r.t. When $ClPMen_2$ was added, the solution was refluxed for another hour. After hydrolysis with degassed 1 M HCl, the mixture was directly evaporated onto silica gel (2 g per 1 g expected product, degassed before use). The coated silica gel was loaded onto the top of a column and chromatography was performed with a gradient PE → PE/Et_2O.

(+)-1-(Dimenthylphosphanyl)-2-(diphenylphosphanyl)benzene (1a):
(2-Bromophenyl)diphenylphosphane (**4**) was prepared by the Pd-catalysed coupling of 1-bromo-2-iodobenzene (which can be obtained by a Sandmeyer reaction of freshly distilled 2-bromoaniline) with (trimethylsilyl)diphenylphosphane following the procedure developed by Stille.[20] To a cooled (–70 °C) solution of **4** (2.09 g, 6.1 mmol) in THF (100 mL) was added dropwise 1.6 M BuLi in hexane (3.85 mL, 6.2 mmol). The solution immediately turned purple. It was stirred for 30 min, when a solution of chlorodimenthylphosphane (2.29 g, 6.64 mmol) in Et_2O (20 mL) was added dropwise. The solution was allowed to warm to r.t. and was stirred under reflux for 15 h. The mixture was then directly evaporated onto silica gel (~ 5 g, degassed before use) and the coated silica gel was loaded onto the top of a silica gel packed column (3×20 cm). The chromatography was performed with a gradient PE → PE/Et_2O 20:1. The solvents were removed to yield 2.3 g of the colourless product **1a** (4.0 mmol, 66%); mp 51–53 °C; R_f(silica gel, PE/Et_2O 20:1) = 0.54.
^{1}H NMR ($CDCl_3$. 400 MHz): δ = 7.75 (cm, ^3J = 7.7 Hz, ^4J = 1.0 Hz, 1 H, H-6), 7.34–7.15 (m, 12 H, H-4, H-5 and PPh_2), 7.07 (ddpt, $^3J_{PH}$ = $^4J_{PH}$ = 3.3 Hz. ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1 H, H-3), 3.13 (cm, 1 H, H_{Men}-8′), 2.18–2.10 (cm, $^3J_{3'ax,2'ax}$ = $^3J_{3'ax,4'ax}$ = 12.1 Hz, $^3J_{3'ax,2'eq}$ = 3.5 Hz, 1 H, H_{Men}-3′$_{ax}$), 1.84 (br d, $^2J_{2'eq,2'ax}$ = 12.7 Hz, 1 H, H_{Men}-2′$_{eq}$), 1.79–1.70 (m, 3 H, H_{Men}-3$_{ax}$, H_{Men}-2$_{eq}$, H_{Men}-6$_{eq}$), 1.62–1.54 (m, 3 H, H_{Men}-5$_{eq}$, H_{Men}-5′$_{eq}$, H_{Men}-6′$_{eq}$), 1.53–1.42 (m, 2 H, H_{Men}-1$_{ax}$,

H_{Men}-8), 1.33–1.25 (m, 1 H, H_{Men}-1′$_{ax}$), 1.23–1.16 (m, 1 H, H_{Men}-4$_{ax}$), 1.11–0.81 (m, $^3J_{7,1} = {}^3J_{7',1'\,=\,6.5\ Hz,\ 3J9',8'} = 6.8$ Hz, 14 H, H_{Men}-4′$_{ax}$, H_{Men}-2′$_{ax}$, H_{Men}-5$_{ax}$, H_{Men}-5′$_{ax}$, H_{Men}-7, H_{Men}-7′, H_{Men}-9′, H_{Men}-6$_{ax}$), 0.76–0.59 (2 dpq + dd, $^3J_{2'ax,3'ax} = {}^3J_{2'ax,1'ax} = 12.5$ Hz, $^3J_{10',8'} = 6.5$ Hz, 5 H, H_{Men}-2′$_{ax}$, H_{Men}-6′$_{ax}$, H_{Men}-10′), 0.47 (d, $^3J_{10,8} = 6.8$ Hz, 3 H, H_{Men}-10), 0.11 (d, $^3J_{9,8} = 6.7$ Hz. 3 H. H_{Men}-9).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 144.5 (dd, J = 9.3 and 34.2 Hz, 1 C, C-1 or C-2), 144.2 (dd, J = 22.7 and 34.5 Hz, 1 C, C-2 or C-1), 139.4 (dd, J = 8.4 and 16.7 Hz, 1 C, C_{quart}-1′), 138.3 (dd, J = 3.1 and 15.7 Hz, 1 C, C_{quart}-1″), 135.7 (dd, J = 7.1 and 2.5 Hz, 1 C, C-3 or C-6), 135.4 (dd, J = 7.5 and 1.0 Hz, 1 C, C-6 or C-3), 133.6 and 133.3 (2 d, ^2J = 19.9 and 18.5 Hz, 4 C, C-2′, C-6′, C-2″, C-6″ of PPh_2), 128.3–128.1 (m, 6 C, C-4 and C-5, C-3′, C-5′, C-3″, C-5″ of PPh_2), 127.7 and 127.2 (2 s, 2 C, C-4′, C-4″ of PPh_2), 49.4 (d, ^2J = 24.0 Hz, 1 C, C_{Men}-4), 42.7 (dd, J = 11.5 and 1.5 Hz, 1 C, C_{Men}-4′), 39.4 (d, ^2J = 3.5 Hz, 1 C, C_{Men}-2), 38.2 (d, ^2J = 5.5 Hz, 1 C, C_{Men}-2′), 36.2–35.7 (m, 2 C, C_{Men}-3, C_{Men}-3′), 34.9 (2 s, 2 C, C_{Men}-6, C_{Men}-6′), 34.0 (d, ^3J = 5.1 Hz, 1 C, C_{Men}-1), 33.7 (s, 1 C, C_{Men}-l′), 28.2 (d, ^3J = 13.1 Hz, 1 C, C_{Men}-8), 27.9 (dd, J = 18.5 and 7.5 Hz, 1 C, C_{Men}-8′), 25.4 (d, ^3J = 11.0 Hz, 1 C, C_{Men}-5), 25.2 (d, ^3J = 8.0 Hz, 1 C, C_{Men}-5′), 23.1 (s, 1 C, C_{Men}-7), 22.7 (d, ^4J = 11.0 Hz, 1 C, C_{Men}-7′), 21.8 and 21.5 (2 s, 2 C, C_{Men}-10, C_{Men}-10′), 15.4 (2 s, 2 C, C_{Men}-9, C_{Men} 9′).

^{31}P NMR ($CDCl_3$, 162 MHz): δ = –13.7 (d, $^3J_{PP} = 156.2$ Hz, PPh_2); –18.5 (d, $^3J_{PP} = 156.2$ Hz, $PMen_2$).

IR (KBr): ν = 3075, 3057 (ar. C-H); 2923, 2868 (al. C-H); 1951; 189l; 1812; 1587; 1575; 1481; 1462, 1445, 1437 (P-ar.); 1385; 1368; 1180; 1087; 736; 685 cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 570.6 (6, M^+), 431.5 (100, $[M–Men]^+$), 293.2 (92, $[M–2xMen]^+$), 215.0 (35, $[M–2xMen–Ph]^+$), 183.0 (74, $[M–2xMen–PhP]^+$).

$[\alpha]_\lambda$ (c = 1, CH_2Cl_2): 15.7 (589 nm), 17.6 (578 nm), 27.6 (546 nm), 161 (436 nm).

$C_{38}H_{52}P_2$	calcd	C	79.96	H	9.18
(570.8)	found		79.79		8.96

(–)-1,2-Bis(dimenthylphosphanyl)benzene (1b):

According to the literature, 1,2-dilithiobenzene (**12**) was prepared from *o*-phenylenemercury (**11**)[47] (5.2 g, 18.8 mmol) in freshly distilled Et_2O (100 mL).[39] The deep purple ethereal solution was shown by the Gilman test to be 77% in organic bound lithium. It can be stored at –30°C for about two weeks without loss of activity.

To a cooled (–60°C) solution of $ClPMen_2$ (4.5 g. 13.0 mmol) in freshly distilled Et_2O (100 mL) was added dropwise the ethereal dilithiobenzene **12** solution (40 mL, 5.7 mmol). The mixture was allowed to warm slowly to r.t. and it was hydrolysed with degassed H_2O. The remaining suspension was distributed between H_2O and Et_2O. While evaporating the organic layer, a pale gray precipitate formed. It was filtered off and characterised as the side-product tetramenthylbisphosphane. The remaining oily residue was dissolved in hexane (20 mL), silica gel was added, and the hexane was removed. The coated silica gel was loaded onto the top ofa flash column (silica gel, 4 × 20 cm) and eluted with PE → PE/Et_2O 20:1. The solvents were removed and the remaining residue was treated with MeOH to give a 1:l mixture of the product **1b** and dimenthylphenylphosphane **1c**, which could not be separated. The mixture was dried in vacuo to yield an off-white solid (1.48 g, 24% calcd rel. to **1b**, 48% calcd rel. to 1:1 mixture); mp 83–86°C.

^{31}P NMR ($CDCl_3$, 162 MHz): δ = –8.4 (s, **1c)**, –l8.4 (s, **1b**) (l:1).

IR (KBr): ν = 3052, 3045 (ar. C-H); 2948, 2918. 2861 (al. C-H); 1452, 1431 (P-ar.);1382; 1367; 1172; 991; 850; 748; 738; 697 cm^{-1}.

MS (FD, CH_2Cl_2): *m/z* = 694.5 (**1b**$^+$), 386.2 (**1c**$^+$).

$[\alpha]_\lambda$ (c = 0.72, CH_2Cl_2): –112 (589 nm), –116 (578 nm), –130 (546 nm).

$C_{46}H_{80}P_2$ **1b**/$C_{26}H_{43}P$ **1c (1:1)**	calcd	C	79.95	H	11.46
(695.1) + (386.6)	found		78.47		11.06

1-Bromo-1′-(diphenylphosphanyl)ferrocene (5a):

According to the General Procedure on a 19.8 mmol scale relative to 1,1′-dibromoferrocene with $ClPPh_2$. Chromatography (alumina, 3 × 20 cm) yielded large orange-red crystals (7.3 g, 16.3 mmol, 82%); mp 104–106°C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.39–7.31 (m, 10 H, PPh_2), 4.42 (t, 2 H, H-3′, H-4′), 4.33 (t, 2 H, H-2, H-5), 4.16 (q, $^3J_{PH} = 1.9$ Hz, 2 H, H-2′, H-5′), 3.99 (t, 2 H, H-3, H-4).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 138.7 (d, ^1J = 9.5 Hz, 2 C, C-1″ of PPh_2), 133.5 (d, ^2J = 19.5 Hz. 4 C, C-2″ of PPh_2), 128.6 (s, 2 C, C-4″ of PPh_2), 128.2 (d, ^3J = 6.9 Hz, 4 C, C-3″ of PPh_2), 77.8 (d, ^1J = 7.8 Hz, 1 C, C-1′), 77.7 (s, 1 C, C-1), 75.0 (d, ^2J = 14.5 Hz, 2 C, C-2′, C-5′), 74.2 (d, ^3J = 3.7 Hz, 2 C, C-3′, C-4′), 71.1 (s, 2 C, C-3, C-4), 68.5 (d, ^nJ = 1.2 Hz. 2 C, C-2, C-5).

^{31}P NMR ($CDCl_3$, 162 MHz): δ = –17.1 (s).

IR (KBr): ν = 3050, 3017 (ar. C-H); 1775; 1641; 1585 (ar. C=C); 1476, 1431 (P-ar.); 1407; 1345; 1155; 1024; 815; 745 cm^{-1}.

MS (FD, CH_2Cl_2):*m/z* = 449.7/447.7 M^+.

$C_{22}H_{18}BrFeP$	calcd	C	58.84	H	4.04	Br	17.80
(449.1)	found		58.78		4.29		17.29

1-Diphenylphosphanyl-1′-iodoferrocene (5b):

Into a flask were placed 1,1′-diiodoferrocene (5.30 g, 12.1 mmol) and $(MeCN)_2PdCl_2$ (77 mg, 0.30 mmol, 0.025 equiv). The flask was evacuated and filled with Ar three times. Enough benzene (20 mL) was added to make a 0.5 M solution ofthe iodo compound and (trimethylsilyl)diphenylphosphane (3.33 mL, 13.0 mmol) was added via syringe. The deep purple solution was heated to 60°C for 5 d. After cooling to r.t., $CHCl_3$ (100 mL) was added. The organic layer was washed with sat. aq $NaHCO_3$, H_2O and brine and dried ($MgSO_4$). Alumina (ca. 10 g) was added, before the solvents were removed. The coated alumina was loaded onto the top of a column (alumina, 3 × 20 cm) and chromatographed with PE → PE/toluene l:0 → 4:l to give successively recovered 1,1′-diiodoferrocene (1.09 g, 21%) and the desired product **5b**, a yellow powder (1.85 g, 38% calcd rel. to converted starting material), mp 82–83°C. With acetone of a third fraction was isolated, identified as 1,1′bis(diphenylphosphanyl)ferrocene (1.30 g. 19%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.39–7.31 (m 10 H. PPh_2), 4.37 (t, 2 H, H-3, H-4), 4.32 (t, 2 H, H-2′, H-5′), 4.12 (q, $^3J_{PH} = 1.8$ Hz, 2 H, H-2, H-5), 4.03 (t, 2 H, H-3′, H-4′).

^{31}P NMR ($CDCl_3$, 162 MHz): δ = –l7.2 (s).

IR (KBr): ν = 3067 (ar. C-H); 1780; 1639; 1585 (ar. C=C); 1477, 1431 (P-ar.); 1403; 1343; 1308; 1159; 1024; 861; 820; 742; 697 cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 496.0 (100, M^+), 369.0 (37, $[M–I]^+$).

$C_{22}H_{18}FeIP$	calcd	C	53.26	H	3.66
(496.1)	found		53.79		3.84

2,2′-Dibromo-1,1′-biphenyl (7):

The brominating agent dibromo(triphenyl)phosphorane Ph_3PBr_2 was prepared in situ from triphenylphosphane (240 g, 0.92 mol) and bromine (153 g, 49 mL, 0.96 mol) in MeCN (500 mL) according to the literature.[26] To the yellowish suspension of Ph_3PBr_2 in MeCN was added in several portions 2,2′-dihydroxy-1,1′-biphenyl (79 g, 0.42 mol). The viscous slurry was stirred at 60°C for 1 h and the solvent was evaporated. Last traces of MeCN were removed in vacuo using a bath temperature of 100°C. The temperature was gradually raised to 280°C by means of a heating mantle over a period of 1 h. At about 140°C the strongly fuming MeCN · HBr adduct was formed and distilled off. At 220°C the melt became clear and evolution of HBr occurred. The temperature of 280°C was kept for 30 min to complete the reaction. After cooling, at a temperature of 100 °C Celite (ca. 200 g) and toluene (300 mL) were added. The suspension was allowed to cool to r.t. under vigorous mechanica1 stirring. It was loaded onto the top of a silica gel column (10 × 10 cm) and the product was separated from triphenylphosphane oxide by filtration. About 2 L of a PE/EtOAc 15:1 mixture were needed to elute the product. The solvents were removed and the resulting viscous yellow residue was recrystallised from EtOH (90 mL) yielding colourless crystals of **7** (63 g, 0.2 mol, 48%); mp 74–76°C; R_f (silica gel, toluene) = 0.7; R_f (silica gel, PE/toluene) = 0.65.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.69–7.66 (m, 2 H, H-3,3′), 7.40 –7.35 (m, 2 H, H-5,5′), 7.28–7.23 (m, 4 H, H-4,4′, H-6,6′).
IR (KBr): ν = 3056 (ar. C-H); 1453, 1426 (P-ar.); 1025; 1003; 758; 724; 668 cm^{-1}.
MS (EI, 70 eV): *m/z* (%) = 313.6/311.6/309.6 (8/17/9, M^+), 232.7/ 230.7 (31/32, $[M\text{-}Br]^+$), 151.9 (100, $[M\text{-}2Br]^+$).

$C_{12}H_8Br_2$	calcd	C	46.20	H	2.58	Br	51.22
(312.0)	found		46.01		2.68		51.20

2-Bromo-2′-(diphenylphosphanyl)-1,1′-biphenyl (8):
According to the General Procedure on a 57 mmol scale relative to **7** with $ClPPh_2$. After chromatography (silica gel, 5 × 30 cm) a colourless, fluffy solid **8** (8.7 g, 20.8 mmol, 49%) was obtained; mp l05–107°C; R_f(silica gel, PE/Et_2O 30:1) = 0.37.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.63 (dd, $^3J_{3,4}$ = 7.8 Hz, $^4J_{3,5}$ = 1.6 Hz, 1 H, H-3), 7.42 (dpt, $^3J_{5',4'}$ = 7.3 Hz $^3J_{5',6'}$= 7.6 Hz, $^4J_{5',3'}$ = 1.6 Hz, 1 H, H-5′), 7.33 (dpt, $^3J_{4',3'}$ = 6.6 Hz, $^3J_{4',5'}$ = 7.3 Hz, $^4J_{4',6'}$ = 1.7 Hz, 1 H, H-4′), 7.32–7.20 (m, 10 H, PPh_2), 7.24 (dd, $^3J_{6',5'}$ = *7.6* Hz, $^4J_{6',4'}$ = *1.7 Hz, 1 H, H-6′), 7.16* (dpt, $^3J_{4,3}$ = 7.8 Hz, ^3J4,5 = 7.3 Hz, $^4J_{4,6}$ = 1.9 Hz, 1 H, H-4), 7.14 (ddd, $^3J_{PH}$ = 3.7 Hz, $^3J_{3',4'}$ = 6.6 Hz, $^4J_{3',5'}$ = 1.6 Hz, 1 H, H-3′), 7.12 (dpt, $^3J_{5,4}$ = $^3J_{5,6}$ = 7.3 Hz, $^4J_{5,3}$ = 1.6 Hz, 1 H, H-5), 6.96 (dd, $^3J_{6,5}$ = 7.3 Hz. $^4J_{6,4}$ = 1.9 Hz, 1 H, H-6).

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 147.0 (d, ^2J = 31.0 Hz, 1 C, C-l′), 142,0 (d, ^3J = 6.6 Hz, 1 C, C-1), 137.2 (d, ^1J = 12.0 Hz, 1 C, C-2′), 136.8 and 136.9 (2 d, ^1J = 12.3 and 11.8 Hz, 2 C, C-1″ of PPh_2), 133.6 and 133.9 (2 d, ^2J = 19.6 and 20.1 Hz, 4 C, C-2″, C-6″ of PPh_2), 133.8 (d, ^2J = 1.2 Hz, 1 C, C-3′), 132.3 (s, 1 C, C-3), 131.8 (d, ^4J = 3.5 Hz, 1 C. C-6), 129.9 (d, ^3J = 5.4 Hz, 1 C, C-6′), 129.0 (s, 1 C, C-4), 128.6 and 128.7 (2 s, 2 C, C-4″ of PPh_2), 128.3 (2 d, ^3J = 2.6 and 2.8 Hz, 4 C, C-3″, C-5″ of PPh_2), 128.3 (d, ^4J = 2.8 Hz, 1 C, C-5′), 128.1 (s, 1 C, C-4′), 126.4 (s, 1 C, C-5), 124.0 (d. ^4J = 1.9 Hz, 1 C. C-2).
^{31}P NMR ($CDCl_3$, 162 MHz): δ = –12.5 (s).

IR (KBr): ν = 3054. 3005 (ar. C-H); 1584; 1562 (ar. C=C); 1478; 1454, 1430 (P-ar.); 1088; 1026; 1002; 765; 745; 696 cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 417.1/415.1 (l/1%, $[M\text{-}H]^+$), 337.1 (100%, $[M\text{-}Br]^+$), 260.1 (5%, $[M\text{-}Br\text{-}Ph]^+$), 182.9 (16%, $[M\text{-}Br\text{-}2xPh]^+$).

$C_{24}H_{18}BrP$	calcd	C	69.08	H	4.35
(417.3)	found		68.25		4.42

(–)-1-Dimenthylphosphanyl-1′-(diphenylphosphanyl)ferrocene (2a):
MethodA: Via Nucleophilic P–C bond opening of(1,1'-Ferrocenediyl)phenylphosphane **6** *with PhLi:*
To a solution of 20% PhLi in hexane/Et_2O (7:3) (1.5 mL, 3 mmol) in Et_2O (5 mL) was added over 45 min at r.t. a solution of **6** (0.8 g, 2.7 mmol) in hexane (50 mL). After stirring for 1 h, the solvent was removed. The brown orange residue was dissolved in freshly distilled THF (20 mL) and cooled to –50°C. A solution of $ClPMen_2$ (1.18 g, 3.4 mmol) in THF (30 mL) was added over 45 min and the reaction mixture was allowed to warm up. It was refluxed for an additional hour and after cooling hydrolysed with degassed 1 M HCl (0.5 mL). Silica gel (ca. 3 g) was added and the solvents were removed. The coated silica gel was loaded onto the top ofa column (alumina, 3 × 15 cm) and chromatographed with hexane → hexane/Et_2O (40:1) to yield the product **2a** (0.55 g, 0.8 mmol, 36%).

Method B: Via Halogen–Metal Exchange with 1-Bromo-1′-(diphenylphosphanyl)ferrocene (**5a**) *and t-BuLi:*
5a (3.40 g, 7.57 mmol) was dissolved in freshly distilled Et_2O (100 mL) and cooled to –78°C. 1.6 M t-BuLi in pentane (5 mL, 8 mmol) was added dropwise over 15 min and the reaction mixture was stirred for 30 min at –70°C. Then a solution of$ClPMen_2$ (2.74 g, 7.94 mmol) in freshly distilled THF (10 mL) was added and the cooling bath was removed. The mixture was refluxed for another hour and hydrolysed with degassed sat. brine (1 mL). Then it was directly evaporated onto silica gel (10 g). Chromatography (alumina, 2.5 × 20 cm) with PE yielded the orange-red solid **2a** (2.45 g, 3.6 mmol, 48%) which was recrystallised from hexane (10 mL); mp 14l–l42°C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.43–7.29 (m, 10 H, PPh_2), 4.42–4.41 (m, 1 H, H_{Fc}), 4.38–4.37 (m, 1 H, H_{Fc}), 4.24–4.22 (cm, 1 H, H_{Fc}), 4.15–4.12 (m, 3 H, H_{Fc}), 4.07–4.05 (cm, 1 H, H_{Fc}), 3.93 (cm, 1 H. H_{Fc}), 2.83–2.68 (cm. $^4J_{PH}$ = 7.0 Hz, $^3J_{8,10}$ = $^3J_{8,9}$ = $^3J_{8',10'}$ = $^3J_{8',9'}$ = 6.9 Hz, 2 H, H_{Men}-8, H_{Men}-8′), 2.02 (br d, $^2J_{2eq',2ax'}$ = 12.9 Hz, 1 H, H_{Men}-2′$_{eq}$), 1.85 (pt, $^3J_{3ax,4ax}$ = $^3J_{3ax,2ax}$ = 11.2. Hz, 1 H, H_{Men}-3$_{ax}$), 1.79–1.76 (m, 2 H, H_{Men}-6$_{eq}$, H_{Men}-5$_{eq}$), 1.68–1.60 (m, 2 H, H_{Men}-6′$_{eq}$, H_{Men}-5′$_{eq}$), 1.38–0.88 (m $^3J_{10,8}$ = $^3J_{10',8'}$ = 6.8 Hz, $^3J_{7,1}$ = 6.5 Hz, 19 H. H_{Men}-1$_{ax}$, H_{Men}-3′$_{ax}$, H_{Men}-2$_{eq}$, H_{Men}-1′$_{ax}$, H_{Men}-4′$_{ax}$, H_{Men}-2′$_{ax}$, H_{Men}-4$_{ax}$, H_{Men}-6$_{ax}$, H_{Men}-5$_{ax}$, H_{Men}-5′$_{ax}$, H_{Men}-7. H_{Men}-10, H_{Men}-10′), 0.84 (d, $^3J_{9,8}$ = 6.9 Hz, 3 H, H_{Men}-9), 0.75–0.66 (dpq+dd, 7 H, $^3J_{9',8'}$ = 6.9 Hz, $^3J_{7'1'ax}$ = 6.5 Hz, H_{Men}-6′$_{ax}$, H_{Men}-9′, H_{Men}-7′), 0.41 (dpq, $^4J_{PH}$ = 3.6 Hz, $^3J_{2'ax,3'ax}$ = $^3J_{2'ax,1'ax}$ – $^2J_{2'ax,2'eq}$ = 12.5 Hz, 1 H, H_{Men}-2$_{ax}$).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 139.3 and 139.1 (2 d, ^1J = 9.8 Hz, 2 C, C_{Ph}-1, C_{Ph}-1′), 133.7 and 133.2 (2 d, ^2J = 19.7 and 19.0 Hz, 4 C, C_{Ph}-2, C_{Ph}-2′, C_{Ph}-6, C_{Ph}-6′), 128.5 and 128.3 (2 s, 2 C, C_{Ph}-4, C_{Ph}-4′), 128.1 and 128.0 (2 d, ^3J = 1.8 Hz, 4 C, C_{Ph}-3, C_{Ph}-3′, C_{Ph}-5, C_{Ph}-5′), 78.5 (d, ^1J = 20.3 Hz, 1 C, C_{Fc}-1 or C_{Fc}-1′), 76.0 (d, J = 30.0 Hz, 1 C, C_{Fc}), 75.8 (d, ^1J = 6.4 Hz, 1 C, C_{Fc}-1′ or C_{Fc}-1), 73.9 (d, J = 17.2 Hz, 1 C, C_{Fc}), 73.1 (d, J = 12.3 Hz, 1 C, C_{Fc}), 73.0 (t, J = 3.1 Hz, 1 C, C_{Fc}), 72.6 (dd, J = 4.4 Hz, J = 1.8 Hz, 1 C, C_{Fc}), 71.1 (d, J = 7.7 Hz, 1 C, C_{Fc}), 70.8 (d, J = 1.8 Hz, 1 C, C_{Fc}), 70.3 (d, J = 2.1 Hz, 1 C, C_{Fc}), 46.7 and 44.7 (2 d, ^3J = 21.9 and 14.3 Hz, 2 C, C_{Men}-4, C_{Men}-4′), 40.6 and 39.2 (2 d, ^3J = 3.3 and 2.6 Hz, 2 C, C_{Men}-2, C_{Men}-2′), 38.0 and 34.6 (2 d, ^2J = 15.6 and 23.9 Hz, 2 C, C_{Men}-3, C_{Men}-3′), 35.1 and 35.0 (2 s, 2 C, C_{Men}-6, C_{Men}-6′), 33.8 and 33.6 (2 s, 2 C, C_{Men}-1, C_{Men}-l′), 27.9 and 27.6 (2 d, ^4J = 3.0 and 2.4 Hz, 2 C, C_{Men}-8, C_{Men}-8′), 25.7 (s, 1 C, C_{Men}-5), 25.6 (d, ^4J = 2.5 Hz, 1 C, C_{Men}-5′), 22.8 and 22.7 (2 s, 2 C, C_{Men}-7, C_{Men}-7′), 22.1 and 21.6 (2 s, 2 C, C_{Men}-10, C_{Men}-10′), 16.0 and 15.6 (2 s, 2 C, C_{Men}-9, C_{Men}-9′).
^{31}P NMR ($CDCl_3$, 162 MHz): δ = –16.3 (s, PPh_2), –24.2 (s, $PMen_2$).
IR (KBr): ν= 3103, 3076 (ar. C-H); 2961, 2919, 2863 (al. C-H); 1456, 1439 (P-ar.); 1380; 1161; 1091; 1030; 825; 741; 695 cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 678.6 (54, M^+), 539.5 (33, $[M\text{–}Men]^+$), 493.6 (25, $[M\text{–}PPh_2]^+$), 401.3 (100, $[M\text{–}2xMen]^+$), 216.0 (24, $[M\text{–}2xMen\text{–}PPh_2]^+$).

$[\alpha]_\lambda$ (c = 0.5, CH_2Cl_2): –99 (589 nm), –94 (578 nm), –44 (546 nm).

$C_{30}H_{46}FeP_2$	calcd	C	74.33	H	8.32	
(678.7)	found		74.32		8.63	(*Method A*)
	found		74.24		8.24	(*Method B*)

(–)-1,1′-Bis(dimenthylphosphanyl)ferrocene (2b):
To a cooled (–78°C) suspension of 1,1′-dilithioferrocene–TMEDA adduct[37] (2.21 g, 7.04 mmol) in petroleum ether (bp 80–110°C, 100 mL) was added dropwise a solution of $ClPMen_2$ (6.05 g, 17.5 mmol) in freshly distilled THF (20 mL) over1 h. The solution was allowed to warm up to r.t. and refluxed for 24 h. It was hydrolysed with degassed 1 M HCl (5 mL) and dried (Na^2SO_4). The solvents were removed and the residue was dissolved in CH_2Cl_2 (20 mL). Silica gel (10 g) was added and the CH_2Cl_2 was evaporated. The coated silica gel was added onto the top of a column (alumina, 3 × 20 cm) and eluted with PE → PE/Et_2O (50:1) to give an orange brown solid of **2b** (3.5 g, 4.3 mmol, 62%), mp 190–l93°C (dec.).
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.32–4.31 (cm, 2 H, H_{Fc}, H_{Fc}′), 4.26–4.25 (cm, 2 H, H_{Fc}, H_{Fc}′), 4.19–4.17 (cm, 2 H, H_{Fc}, H_{Fc}′), 4.12–4.11 (cm, 2 H, H_{Fc}, H_{Fc}′), 2.86 (cm. $^4J_{PH}$ = 6.2 Hz, $^3J_{8,10}$ = $^3J_{8,9}$ = 6.8 Hz, 2 H, H_{Men}-8), 2.80 (cm, $^4J_{PH}$ = 6.9 Hz, $^3J_{8',10'}$ = $^3J_{8',9'}$ = 6.8 Hz, 2 H, H_{Men}-8′), 2.13 (br d, $^2J_{2eq,2ax}$ = 12.9 Hz, 2 H, H_{Men}-2$_{eq}$), 1.94 (pt, $^3J_{3ax,4ax}$ = $^3J_{3ax,2ax}$ = 11.4 Hz, $^3J_{3ax,2eq}$ = 2.4 Hz, 2 H, H_{Men}-3$_{ax}$), 1.81–l.78 (m, 4 H, H_{Men}-6$_{eq,\ HMen}$-5$_{eq}$), 1.69–1.60 (m, 4 H, H_{Men}-6′$_{eq}$, H_{Men}-5′$_{eq}$), 1.46–l.35 (m, 6 H, H_{Men}-l$_{ax}$, H_{Men}-3′$_{ax}$, H_{Men}-2′$_{eq}$), 1.25–0.84 (m, $^3J_{7,1}$ = 6.5 Hz, $^3J_{10,8}$ = $^3J_{10',8'}$ = $^3J_{9,8}$ = 6.8 Hz, 38 H, H_{Men}-1′$_{ax}$, H_{Men}-4′$_{ax}$, H_{Men}-2$_{ax}$, H_{Men}-4$_{ax}$, H_{Men}-6$_{ax}$, H_{Men}-5$_{ax}$, H_{Men}-5′$_{ax}$, H_{Men}-7, H_{Men}-10, H_{Men}-10′, H_{Men}-9), 0.73–0.68 (dpq+dd, $^3J_{9',8'}$ = 6.9 Hz, $^3J_{7',1'ax}$ = 6.5 Hz, 14 H, H_{Men}-6′$_{ax}$, H_{Men}-9′, H_{Men}-7′), 0.51 (dpq, $^4J_{PH}$ = 3.3 Hz. $^3J_{2'ax,3'ax}$ = $^3J_{2'ax,1'ax}$ = $^2J_{2'ax,2'eq}$ = 12.8 Hz, 2 H, H_{Men}-2′$_{ax}$).
P NMR ($CDCl_3$, 162 MHz): δ = –24.1 (s).
IR (KBr):[3] = 3096 (ar. C-H); 2956, 2926, 2870, 2853 (al. C-H); 2662; 1457 (P-ar.); 1379; 1369; 188; 155; 1032; 820 cm^{-1}.

MS (FD, toluene): m/z = 803.3 M^+.
$[\alpha]_\lambda$ (c = 1, CH_2Cl_2): –147 (589 nm), –139 (578 nm), –78 (546 nm)

$C_{50}H_{84}FeP_2$	calcd	C	74.79	H	10.54
(803.0)	found		74.63		10.69

(–)-Dimenthylphosphanylferrocene (2c):
Tributylstannylferrocene (10) (1.34 g, 2.8 mmol) was dissolved in freshly distilled THF (15 mL) and cooled to –78°C. Then 1.6 M BuLi in hexane (1.9 mL, 3.0 mmol) was slowly added over 10 min, and the reaction mixture was stirred for 20 min. A precipitate of lithioferrocene appeared. A solution of $ClPMen_2$ (1.08 g, 3.1 mmol) in THF (10 mL) was then added and the cooling bath was removed. At ca. –50°C the colour ofthe mixture turned brown. The solution was heated under reflux for another hour. then cooled to r.t. and hydrolysed with degassed 1 M HCl (1 mL). This mixture was then directly evaporated onto silica gel (~ 5 g, degassed before use) and the coated silica gel was loaded onto the top of an alumina column (3 × 20 cm). First with PE traces of ferrocene were eluted, then with PE/Et_2O (20:1) the product **2c.** The solvents were removed and the remaining oily residue was recrystallised from a minimum of pentane (4 mL) to give red coffinlike crystals (0.60 g, 1.2 mmol, 43%); mp 119.5–121°C.
^{1}H NMR ($CDCl_3$, 400 MHz): δ= 4.30–4.28 (cm, 1 H, H_{Fc}), 4.28–4.26 (cm, 1 H, H_{Fc}), 4.22–4.20 (cm, 1 H, H_{Fc}), 4.17 (s, 5 H, Cp), 4.15–4.14 (cm, 1 H, H_{Fc}), 2.85 (cm, $^4J_{PH}$ = 6.8 Hz, $^3J_{8,10} = {}^3J_{8,9}$ = 6.9 Hz, 1 H, H_{Men}-8), 2.76 (cm, J_{PH} = 6.8 Hz, $^3J_{8',10'} = {}^3J_{8',9'}$ = 6.9 Hz, 1 H, H_{Men}-8′), 2.15 (br d, $^2J_{2eq,2ax}$ = 13.1 Hz, 1 H, H_{Men}-2_{eq}), 1.96 (pt, $^3J_{3ax,4ax} = {}^3J_{3ax,2ax}$ = 11.3 Hz, $^3J_{3ax,2eq}$ = 2.5 Hz, 1 H, H_{Men}-3_{ax}), 1.81–1.78 (m, 2 H, H_{Men}-6_{eq}, H_{Men}-5_{eq}), 1.69–1.60 (m, 2 H, H_{Men}-6′$_{eq}$, H_{Men}-5′$_{eq}$), 1.47–1.37 (m, 3 H, H_{Men}-1_{ax}, H_{Men}-3′$_{ax}$, H_{Men}-2_{eq}), 1.27–1.10 (m, 4 H, H_{Men}-1′$_{ax}$, H_{Men}-4′$_{ax}$, H_{Men}-2′$_{ax}$, H_{Men}-4_{ax}), 1.10–0.88 (m. 15 H, $^3J_{7,1} = {}^3J_{10.8} - {}^3J_{10'.8'} = {}^3J_{9,8}$ = 6.9 Hz, H_{Men}-6_{ax}, H_{Men}-5_{ax}, H_{Men}-5′$_{ax}$, H_{Men}-7, H_{Men}-10, H_{Men}-10′, H_{Men}-9), 0.74–0.68 (dpq+dd, 7 H, $^3J_{9',8'}$ = 6.9 Hz, $^3J_{7',1'ax}$ = 6.5 Hz, H_{Men}-6′$_{ax}$, H_{Men}-9′, H_{Men}-7′), 0.51 (dpq, $^4J_{PH}$ = 3.4 Hz, $^3J_{2'ax,3'ax} = {}^3J_{2'ax,1'ax} = {}^2J_{2'ax.2'eq}$ = 13.0 Hz, 1 H, H_{Men}-2′$_{ax}$).
^{31}P NMR ($CDCl_3$, 162 MHz): δ = –23.3 (s).
IR (KBr): ν = 3099 (ar. C-H); 2956, 2925, 2864 (al. C-H); 1458 (P-ar.); 1413; 1384; 1367; 1191; 1155; 1108; 817 cm^{-1}.
MS (EI, 70 eV): *m/z* (%) = 494.4 (100, M^+).
$[\alpha]_\lambda$ (*c* = 0.45, CH_2Cl_2): –197 (589 nm), –184 (578 nm), –139 (546 nm).

$C_{30}H_{47}FeP$	calcd	C	72.87	H	9.58
(494.5)	found		72.95		9.63

(–)-1-Bromo-1′-(dimenthylphosphanyl)ferrocene (2d):
According to the General Procedure on a 6.0 mmol scale of 1,1′-dibromoferrocene with chlorodimenthylphosphane. Chromatography (alumina, 3 × 15 cm) with PE yielded a viscous red oil of **2d** (2.3 g, 4.0 mmol, 67%) which crystallised over several months.
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.39–4.37 (m, 2 H, H_{Fc}), 4.35–4.34 (m, 1 H, H_{Fc}), 4.32 - 4.31 (m, 1 H, H_{Fc}), 4.24–4.22 (m, 1 H, H_{Fc}), 4.12–4.10 (m, 3 H, H_{Fc}), 2.88–2.74 (cm, $^4J_{P,8}$ = 6.5 Hz, $^4J_{P,8'}$ = 7.0 Hz, $^3J_{8,10} = {}^3J_{8,9} = {}^3J_{8',10'} = {}^3J_{8',9'}$ = 6.9 Hz, 2 H, H_{Men}-8, H_{Men}-8′), 2.14 (br d, $^2J_{2eq,2ax}$ = 13.1 Hz, 1 H, H_{Men}-2_{eq}), 2.02 (pt, $^3J_{3ax,4ax} = {}^3J_{3ax,2ax}$ = 11.4 Hz, $^3J_{3ax,2eq}$ = 2.7 Hz, 1 H, H_{Men}-3_{ax}), 1.81–1.78 (m, 2 H, H_{Men}-6_{eq}, H_{Men}-5_{eq}), 1.69–1.61 (m, 2 H, H_{Men}-6′$_{eq}$, H_{Men}-5′$_{eq}$), 1.48–1.30 (m, 3 H, H_{Men}-1_{ax}, H_{Men}-3′$_{ax}$, H_{Men}-2_{eq}), 1.27–0.83 (m, 19 H, $^3J_{7,1} = {}^3J_{10,8} = {}^3J_{10'.8'} = {}^3J_{9,8}$ = 6.8 Hz, H_{Men}-1′$_{ax}$, H_{Men}-4′$_{ax}$, H_{Men}-2′$_{ax}$, H_{Men}-4_{ax}, H_{Men}-6_{ax}, H_{Men}-5_{ax}. H_{Men}-5′$_{ax}$, H_{Men}-7, H_{Men}-10, H_{Men}-10′, H_{Men}-9), 0.73–0.68 (dpq+dd, $^3J_{9',8'}$ = 6.9 Hz. $^3J_{7',1'ax}$ = 6.5 Hz, 7 H, H_{Men}-6′$_{ax}$, H_{Men}-9′, H_{Men}-7′), 0.49 (dpq, $^4J_{PH}$ = 3.2 Hz, $^3J_{2'ax,3'ax} = {}^3J_{2'ax,1'ax} = {}^2J_{2'ax,2'eq}$ = 12.5 Hz, 1 H, H_{Men}-2′$_{ax}$).
^{31}P NMR ($CDCl_3$, 162 MHz): δ = –24.4 (s).
IR (CH_2Cl_2): ν = 3042 (ar. C-H); 2982, 2953, 2921 (al. C-H); 1500; 1439 (P-ar.); 1417; 1260; 1149; 886; 720 cm^{-1}.
MS (EI, 70 eV): *m/z* (%) = 574.3/572.3 (26/28, M^+), 494.4 (22, $[M–Br]^+$), 436.2/434.2 (12/11, $[M–Men]^+$), 372.3 (54, $[M+O-Br–Men]^+$), 356.2 (8, $[M–Br–Men]^+$), 296.9/294.9 (79/85, $[M–2xMen]^+$), 216.9 (100, $[M–Br–2xMen]^+$).

$[\alpha]_\lambda$ (*c* = 0.9, CH_2Cl_2): –71 (589 nm), –66 (578 nm), –25 (546 nm).

$C_{30}H_{46}BrFeP$	calcd	C	62.84	H	8.32
(573.4)	found		62.56		8.14

(–)-5-P-Menthyl-5H-dibenzophosphole (3c):
A solution of 2.2′-dibromo-1,1′-biphenyl (**7**) (1.29 g, 4.13 mmol) in Et_2O (15 mL) was cooled to 0°C and treated with 1.6 M BuLi in hexane (5.5 mL, 8.8 mmol) to give 2,2′-dilithio-1,1′-biphenyl.[49] The black solution was stirred for 5 h at r.t. and cooled to –15 °C. When a solution of $ClPMen_2$ (3.39 g, 9.8 mmol) in THF (30 mL) was added, the colour turned purple. After stirring for 15 h, it was hydrolysed with degassed 1 M HCl (1 mL). The mixture was directly evaporated onto silica gel (ca. 5 g, degassed before use) and the coated silica gel was loaded onto the top of a silica gel column (3 × 20 cm). The chromatography was performed with PE to yield the colourless solid **3c** (0.35 g, 1.1 mmol. 26%); mp 111–113°C; R_f(silica gel, PE) = 0.75.
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.95–7.92 (m, $^4J_{PH}$ = 0.8 Hz, ^3J = 7.4 Hz, 2 H. H-1, H-9), 7.66 (dddd, $^3J_{PH}$ = 7.4 Hz, $^3J_{4,3}$ = 7.4 Hz, $^4J_{4,2}$ = 1.3 Hz, $^5J_{4,1}$ = 0.8 Hz, 1 H, H-4), 7.61 (dddd, $^3J_{PH}$ = 7.4 Hz, $^3J_{6,7}$ = 7.4 Hz, $^4J_{6,8}$ = 1.3 Hz, $^5J_{6,9}$ = 0.8 Hz, 1 H, H-6), 7.45 (ddd, $^3J_{2,3} = {}^3J_{2,1}$ = 7.4 Hz, $^4J_{2,4}$ = 1.3 Hz, 1 H, H-2), 7.44 (ddd, $^3J_{8,7} = {}^3J_{8,9}$ = 7.4 Hz, $^4J_{8,6}$ = 1.3 Hz, 1 H, H-8), 7.35 (dddd, $^4J_{PH}$= 2.8 Hz, $^3J_{3,2} = {}^3J_{3,4}$= 7.4 Hz, $^4J_{3,1}$ = 1.1 Hz, 1 H, H-3), 7.33 (dddd, $^4J_{PH}$ = 2.8 Hz, $^3J_{7,8} = {}^3J_{7,6}$ = 7.4 Hz, $^4J_{7,9}$ = 1.1 Hz, 1 H, H-7), 3.05 (dddd, $^4J_{PH}$ = 6.9 Hz, $^3J_{8,4ax}$ = 2.9 Hz, $^3J_{8,9}$ = 6.8 Hz, $^3J_{8,10}$ = 6.9 Hz, 1 H, H_{Men}-8), 2.04 (dddd, $^2J_{PH}$ = 8.8 Hz, $^3J_{3ax,2ax} = {}^3J_{3ax,2ax}$ = 11.7 Hz, $^3J_{3ax,2eq}$ = 3.2 Hz, 1 H, H_{Men}-3_{ax}), 1.77 (cm, $J_{5eq,5ax}$ = 12.9 Hz, $^3J_{5eq,4ax}$ = 3.2 Hz, $^3J_{5eq,6ax}$ = 3.6 Hz, 1 H. H_{Men}-5_{eq}), 1.60 (br d. $^2J_{6eq,6ax}$ = 12.9 Hz, 1 H. H_{Men}-6_{eq}), 1.47 (ddddd, $^3J_{PH}$ = 3.7 Hz, $^3J_{4ax,3ax}$ = 11.7 Hz, $^3J_{4ax,5eq}$ = 3.2 Hz, $^3J_{4ax,5ax}$ = 12.0 Hz, $^3J_{4ax,8}$ = 2.9 Hz, 1 H, H_{Men}-4), 1.17 - 1.01 (m, $^3J_{9,8}$ = 6.8 Hz, $^3J_{1,8}$ = 6.9 Hz, 8 H, H_{Men}-l, H_{Men}-5_{ax}, H_{Men}-9, H_{Men}-10), 0.76 (dddd. $^3J_{PH}$ = 2.3 Hz, $^2J_{2eq,2ax}$ = 13.3 Hz, $^3J_{2eq,1ax}$ = 2.3 Hz, $^3J_{2eq,3ax}$ = 3.2 Hz, 1 H, H_{Men}-2_{eq}), 0.66 (dpq, $^2J_{6ax,6eq}$ = 12.9 Hz, $^3J_{6ax,1ax}$ = 11.8 Hz, $^3J_{6ax,5eq}$ = 3.6 Hz, 1 H, H_{Men}-6_{ax}), 0.48 (d, $^3J_{7,1ax}$ = 6.5 Hz, 3 H, H_{Men}-7), 0.02 (dpq, $^3J_{PH}$ = 3.9 Hz, $^2J_{2ax,2eq}$ = 13.3 Hz, $^3J_{2ax,3ax} = {}^3J_{2ax,1ax}$ = 11.7 Hz, 1 H, H_{men}-2_{ax}).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 144.5 and 144.3 (2 d, ^2J = 1.9 and 2.5 Hz, 2 C, C-1a and C-9a), 142.3 and 140.6 (2 d, ^1J = 5.0 and 9.7 Hz, 2 C, C-4a and C-6a), 130.5 and 129.5 (2 d, ^2J = 20.2 and 21.5 Hz, 2 C, C-4 and C-6), 127.9 and 127.8 (2 s, 2 C, C-2 and C-8), 127.0 and 126.6 (2 d, ^3J = 7.2 and 7.0 Hz, 2 C, C-3 and C-7), 121.3 and 121.1 (2 s, 2 C, C-1 and C-7), 45.6 (d, ^2J = 8.0 Hz, 1 C, C_{Men}-4), 41.6 (d, ^1J = 20.5 Hz, 1 C, C_{Men}-3), 35.3 (d, ^2J = 5.2 Hz, 1 C, C_{Men}-2), 34.9 (s, 1 C, C_{Men}-6), 33.5 (d, ^3J = 2.3 Hz, 1 C, C_{Men}-1), 28.9 (d, ^3J = 19.7 Hz, 1 C, C_{Men}-8), 25.7 (d, ^3J = 8.0 Hz, 1 C, C_{Men}-5), 22.1 (s, 1 C, C_{Men}-7), 21.5 (s, 1 C, C_{Men}-l0), 15.5 (s, 1 C, C_{Men}-9).
^{31}P NMR ($CDCl_3$, 162 MHz): δ = –7.5 (s).
IR (KBr): ν = 3070 (ar. C-H); 2954, 2931, 2867 (al. C-H); 1938; 1903; 1594 (ar. C=C); 1456, 1434 (P-ar.); 1366; 1184; 1124; 1082; 1030; 999; 973; 934; 854; 803; 743; 721 cm^{-1}.
MS (EI, 70 eV): *m/z* (%) = 322.2 (88, M^+), 307.1 (4, $[M–Me]^+$), 279.1 (7. $[M–Me–{}^iPr]^+$), 183.9 (100, $[M–Men]^+$).
$[\alpha]_\lambda$ (*c* = 0.88, CH_2Cl_2): –121 (589 nm), –127, (578 nm), –146 (546 nm), –268 (436 nm), –492 (365 nm).

$C_{22}H_{27}P$	calcd	C	81.95	H	8.44
(322.4)	found		80.74		8.16

Side-Product (–)-Tetramenthylbisphosphane:
When trying to prepare **1a** via the Grignard route, a white undissolved residue remained between the aqueous and ethereal layer. This residue was isolated, washed several times with Et_2O and dried in vacuo. Also in the synthesis of **1b**, tetramenthylbisphosphane appeared as a side-product, which could be isolated in ca. 5% yield. The off-white residue is insoluble in Et_2O, slightly soluble in less polar solvents; mp < 240°C (dec.).
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.92–2.90 (m, 2 H), 2.77–2.70 (m, 2 H), 2.36–2.27 (m, 4 H), 1.87–1.72 (m, 8 H), 1.53–0.76 (m, ^3J = 6.5 Hz, ^3J = 6.9 Hz, 48 H), 0.71 – 0.68 (2 d, ^3J = 6.8 Hz, 12 H).

^{31}P NMR ($CDCl_3$, 162 MHz): δ = –42.1 (s).
IR (KBr): ν = 2952, 2925, 2866 (al. C-H); 1456 (P-al.); 1369; 1082; 996; 851 cm^{-1}.
MS (EI, 70 eV): *m/z* (%) = 618.6 (100, M^+).
$[\alpha]_\lambda$ (*c* = 0.34, $CHCl_3$): –375 (589 nm), –394 (578 nm), –456 (546 nm), –865 (436 nm).

$C_{40}H_{76}P_2$	calcd	C	77.62	H	12.38
(619.0)	found		76.92		11.89

Catalyses

The hydrogenation of (Z)-α-acetamidocinnamic acid[42] and ketopantolactone,[43] the hydrosilylation of acetophenone with diphenylsilane[44] and the Grignard cross-coupling of 1-phenylethylmagnesium chloride with vinyl bromide[45] were carried out as described in the literature.

The asymmetric hydrogenation of methyl pyruvate was performed as follows: Under an Ar atmosphere the catalyst was formed in situ by mixing $[Rh(cod)Cl]_2$ (10.0 mg, 0.02 mmol; 0.04 mmol Rh) and a bisphosphane ligand (0.044 mmol) (or 0.088 mmol of a monophosphane ligand) in toluene (1 mL) for 5 min. Then a solution of methyl pyruvate (0.75 mL, 8 mmol) in MeOH (10 mL) was placed in a 100 cm^3 stainless steel autoclave. After the atmosphere was replaced with hydrogen, the reaction mixture was stirred for 20 h under 30 bar hydrogen pressure at ambient temperature. Afterevaporation ofthe solvent, the resulting residue was distilled bulb-to-bulb to give methyl lactate. The yield was measured by ^{1}H NMR. The enantiomeric excess was determined by GC analysis (Chirasil-L-Val, 25 m) after converting an aliquot ofthe product to the isopropylcarbamate derivative in CH_2Cl_2.

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