DIFERROCENYLPHOSPHINE: A FACILE SYNTHESIS AND ITS USE TO PREPARE CHIRAL PHOSPHINES

Denis GUILLANEUX, Lars MARTINY and Henri B. KAGAN[1,*]

Laboratoire de Synthèse Asymétrique (UPRESA 8075), Université Paris-Sud, 91405-Orsay, France; e-mail: [1] kagan@icmo.u-psud.fr

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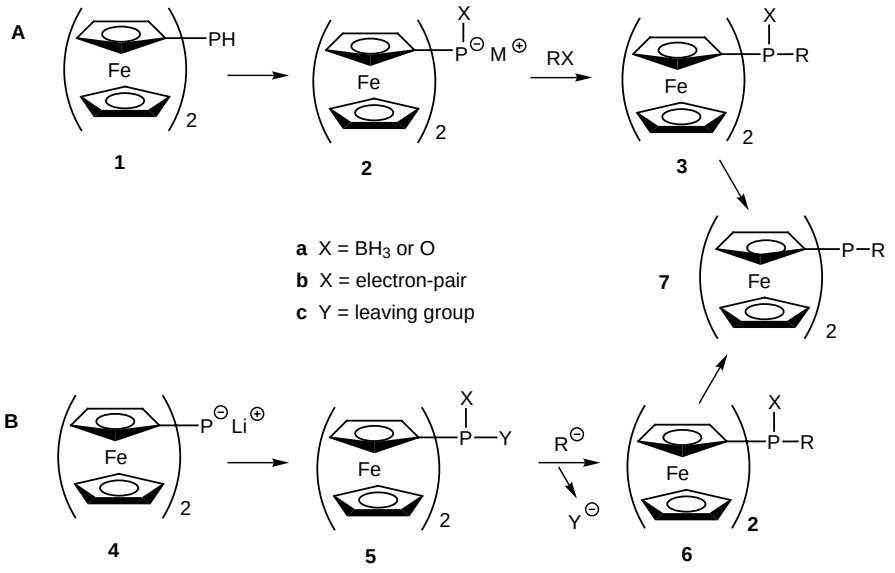
Dedicated to Professor Otakar Červinka on the occasion of his 75th birthday.

Diferrocenylphosphine–borane has been synthesized in three steps from monolithioferrocene. This compound may be transformed into the corresponding phosphide which is a nucleophilic reagent allowing to introduce the diferrocenylphosphino grouping in organic compounds. Several chiral diphosphines related to DIOP have been synthesized by this method. The corresponding rhodium complexes are catalysts in the hydrogenation of various C=C double bonds.

Key words: Diferrocenylphosphine; Ferrocenes; DIOP; P-Ligands; Phosphines; Metallocenes; Chiral ferrocenyldiphosphines; Asymmetric hydrogenation.

There are many examples in literature of chiral ferrocenyl diphosphines useful for asymmetric catalysis (for some reviews see refs[1–5]). By contrast, few examples of chiral phosphines are known where phosphorus is linked to two ferrocene units. Two different methodologies may be envisaged to introduce the diferrocenylphosphino (Fc_2P) moiety in organic molecules to obtain compounds such as **7** (R = chiral group) (Scheme 1). In the first strategy (**A**) the anion of diferrocenylphosphine **1** (protected at P by borane) reacts with a C-electrophile, generating the final product **3**. One may also envisage the reaction of an electrophilic phosphorus compound **5** (protected by BH_3) on a C-nucleophile giving the phosphine **6**. We investigated the both strategies but it is only the approach **A** which was successful and which will be presented here.

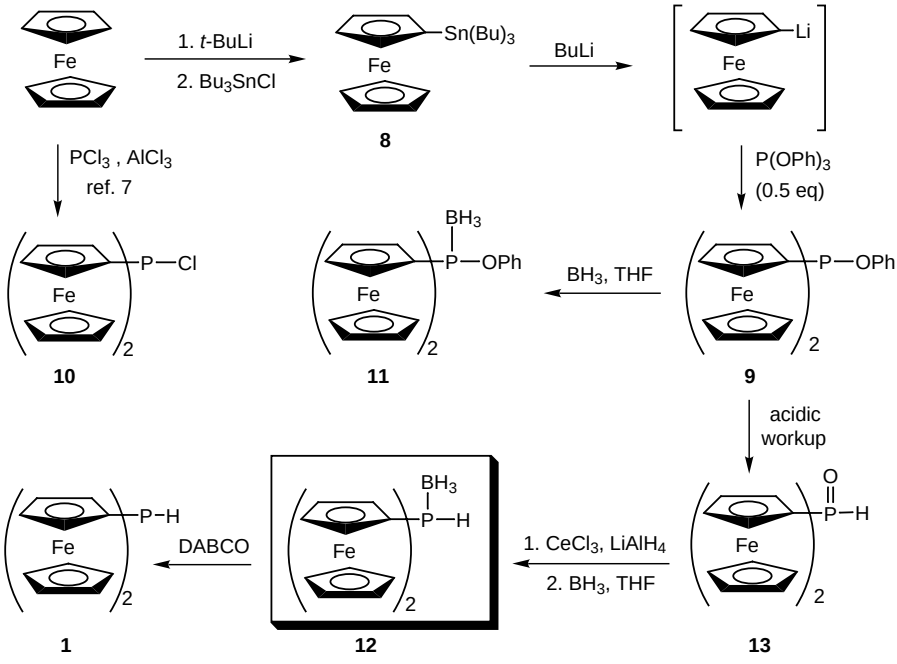
We wish to describe here an efficient preparation of diferrocenylphosphine–borane **12** (Scheme 2) and its usefulness in organic synthesis, as examplified by the synthesis of the chiral diphosphines **17**, **24** and **25** ferrocenyl analogs of DIOP **18**.



SCHEME 1

Synthesis of Diferrocenylphosphine

Diferrocenylphosphine (**1**) may, in principle, be obtained by reduction of diferrocenylchlorophosphine **10** (Scheme 2). This latter has been isolated from electrophilic substitution of ferrocene by PCl_3 in presence of $AlCl_3$; however the yield was lower than 10% because of the poor control of the reaction selectivity[6]. Therefore, we devized an alternate route as illustrated in Scheme 2. We started from tributylstannylferrocene (**8**), which is an excellent stable precursor of monolithioferrocene (ref.[7]). Compound **8** was easily obtained *via* direct lithiation of ferrocene by *t*-BuLi at 30 mmol scale followed by treatment with Bu_3SnCl. Subsequent transmetallation by 1 equivalent of BuLi cleanly generates *in situ* monolithioferrocene, which is then treated with 0.5 equivalent of triphenylphosphite. After acidic hydrolysis, diferrocenylphosphine oxide (**13**) was isolated in 59% overall yield. This compound was reduced to diferrocenylphosphine with $CeCl_3$–$LiAlH_4$ which was introduced by Imamoto for the reduction of phosphine oxides[8]. Addition of BH_3 in THF afforded temporary protection of phosphorus and facilitated the isolation procedure. Diferrocenylphosphine–borane adduct **12** was thus obtained in 88% yield as an air-stable compound. Phenyl diferrocenylphosphinite (**11**) was isolated in 68% yield as the borane derivative. However, it could not be easily transformed into **12**. Diferrocenylphosphine **1** may be quantitatively regenerated from **12** by heating with DABCO.



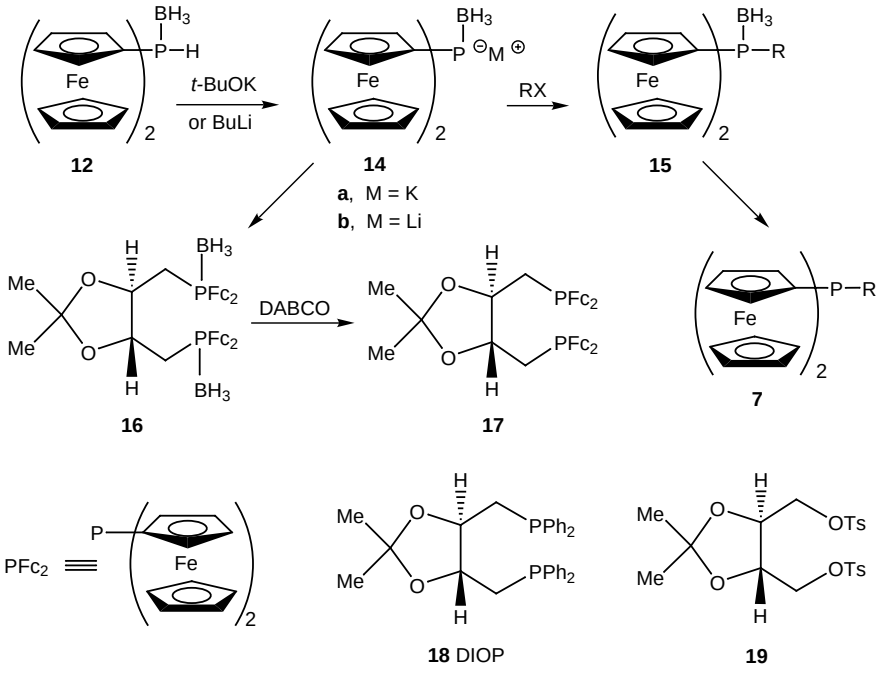
SCHEME 2

Having developed an efficient preparation of diferrocenylphosphine as the protected borane derivative **12**, we turned to the use of this reagent in the preparation of achiral and chiral phosphines.

Synthesis of Diferrocenylphosphine Derivatives

Diferrocenylphosphine–borane (**12**) was conveniently deprotonated *in situ* by *t*-BuOK or BuLi. The resulting phosphides, especially potassium phosphide (**14a**), have nucleophilic properties and may react with various electrophiles (Scheme 3). In this way, diferrocenyl(methyl)phosphine (**7**; R = Me) was easily obtained, after deprotection of the borane adduct **11**. One interesting application of reagent **14a** is its use for the preparation of chiral phosphines by reaction with chiral electrophiles. This will be first illustrated by the synthesis of diphosphine **16**, a tetraferrocenyl analog of DIOP (**18**; 4,5-bis[(diphenylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane).

Chiral (*S*,*S*)-ditosylate **19** (derived from natural (*R*,*R*)-tartaric acid) was added to 3.1 equivalents of potassium salt **14a** prepared *in situ* from phosphine– borane **12** in THF. After 3 h at room temperature and workup, the bis(phosphine–borane) **16** was isolated in 70% as a crystalline compound.



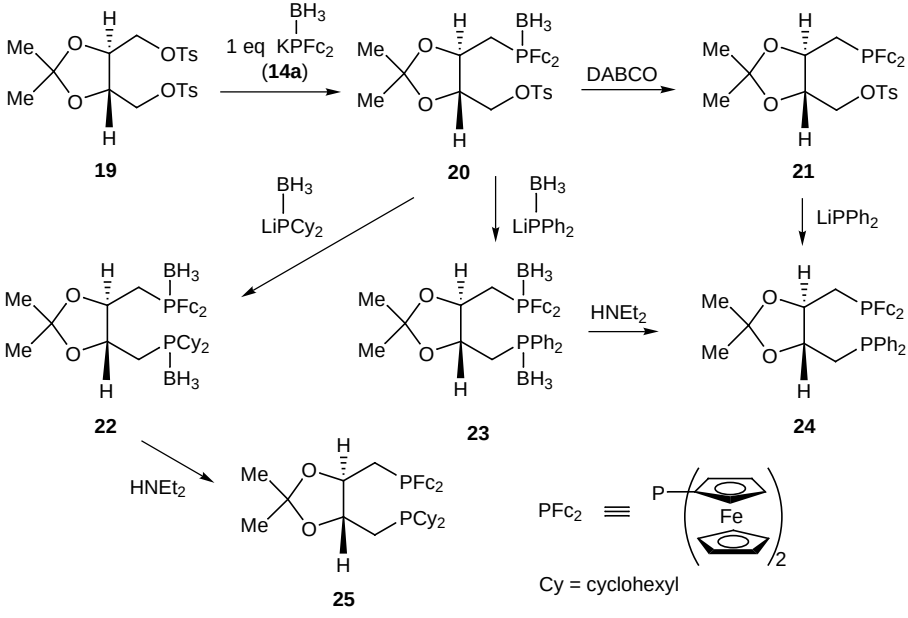
SCHEME 3

Removal of borane by DABCO gave quantitatively the tetraferrocenyl analog of DIOP **17**. This diphosphine is air-stable and its abilility to generate chiral catalysts was briefly investigated (*vide infra*).

Scheme 4 describes the syntheses of other analogs of DIOP prepared from monotosylate **20**, which in turn was readily obtained in 80% yield by the action of one equivalent of phosphorus reagent **14a** with ditosylate **19**.

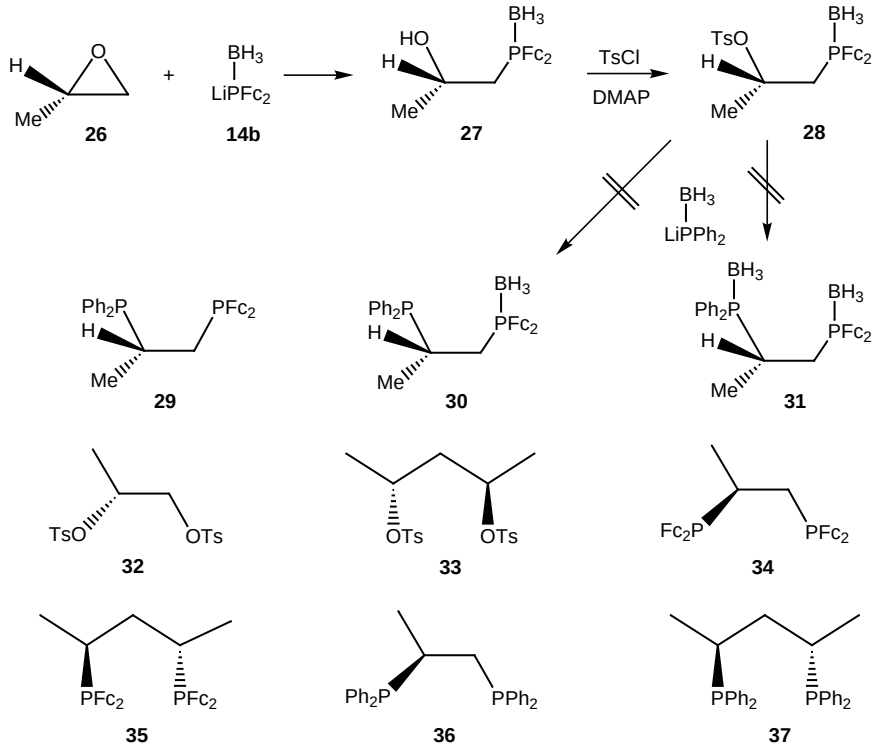
The diferrocenyl analog of DIOP **24** was synthesized from monotosylate **20** in two ways. It is possible to introduce the second phosphorus by action of borane adduct of lithium diphenylphosphide. The resulting bis(phosphine–borane) **23** (75% yield) is then deprotected by heating in diethyl- amine to give diphosphine **24** in 80% yield. The alternate procedure involves the quantitative removal of borane by heating the monotosylate **20** with DABCO. The resulting monotosylate **21** was then treated by $LiPPh_2$ in THF but the expected diphosphine **24** was isolated in only 33% yield. The former procedure is then the preferred one. The reaction of borane adduct of lithium dicyclohexylphosphide ($LiPCy_2$) gave in good yield nucleophilic substitution on monotosylate **20**. The resulting bis(phosphine–borane) **22** was transformed into the desired diphosphine **25** by heating in diethyl-

amine under strictly anaerobic conditions (since **25** is easily oxidized). In that way, diphosphine **25** was isolated in 85% yield. The structures of the two ferrocenyl analogs of DIOP **24** and **25** were easily assigned by NMR spectroscopy. The loss of C_2 symmetry (with respect to DIOP **18** or to its tetraferrocenyl analog **17**) was clearly indicated in the various ^{1}H NMR signals (non-equivalency of the two geminal methyl groups) and in ^{31}P NMR (two different phosphorus). Selected physical data concerning **17**, **24** and **25** are given in the Experimental.



SCHEME 4

Attempts have been made to prepare diferrocenyl analogs **34** and **35** of prophos **36** and skewphos **37** (Scheme 5). Ditosylate **32** was quite unreactive towards reagents **14** giving only partial monosubstitution. Presumably the bulky nucleophilic reagent cannot easily effect the substitution of the tosyloxy group located on a secondary carbon. Therefore, we briefly investigated the epoxide opening by anion **14**, hoping to prepare a diferrocenyl analog **29** of prophos **36**. (*S*)-Methyloxirane (**26**) was transformed into the alcohol **27** in 96% yield. Tosylation (81% yield) gave monotosylate **28**. Unfortunately, $LiPPh_2$ or $LiPPh_2{\cdot}BH_3$ failed to effect the subsequent transformation into diphosphine **30** or **31**. The presence of the vicinal PFc_2 moiety in **28** severely slows down the desired substitution reaction.



SCHEME 5

Preliminary Screening of Rhodium Complexes

There is no indication in the literature of the catalytic behavior of complexes with ligands such as Fc_2PR or Fc_3P. The ferrocenyl group may be considered an electron-rich substituent, more bulky than a phenyl ring.

Diphosphine **17** was able to coordinate to rhodium, notwithstanding the steric hindrance introduced by the four ferrocenyl substituents. Thus, the isolated rhodium complex [Rh(COD)(**17**)·PF_6] has been prepared from diphosphine **17**, [Rh(acac)COD] and NH_4PF_6 (COD = cycloocta-1,4-diene). The cationic rhodium complexes of the three ferrocenyl analogs of DIOP **17**, **24** and **25** were evaluated as catalysts for asymmetric hydrogenation of various C=C double bonds. Despite the bulkiness of PFc_2 moiety the rhodium complexes show good catalytic activities. They can be used (1% of mole equivalent) at room temperature under 1 atm hydrogen pressure, in methanol. However the enantioselectivities are moderate. For example *Z*-2-acetamido-3-phenyl- prop-2-enoic acid has been hydrogenated into

(*R*)-*N*-acetylphenylalanine in the presence of cationic complexes [(Rh(COD)(**17**)], [Rh(COD)(**24**)] and [Rh(COD)(**25**)] with 64, 52 (5 atm H_2) and 12% ee, respectively. Complex [Rh(COD)(**17**)] catalyzed the formation of (*R*)-*N*-acetylphenylalanine methyl ester from its dehydro precursor with an enantioselectivity of 55% ee. The rhodium complex involving **17** as ligand is fairly active (0.5 mole equivalent) in the hydrogenation of itaconic acid, giving (*S*)-methylsuccinic acid (40% ee). It is interesting to see that the absolute configuration of the products is the same when using (*R*,*R*)-**25** or (*R*,*R*)-DIOP **18**. For example **18** gave (*R*)-*N*-acetylphenylalanine in 80% ee[9b].

In conclusion, we described an easy access to diferrocenylphosphine–borane (**12**), a useful reagent for introducing the PFc_2 unit into organic molecules, *i.e.* DIOP analogs **17**, **24** and **25**.

We intend to explore the scope of these ligands in asymmetric catalysis as well as the potential of reagent **12** to prepare various kinds of chiral phosphines with two ferrocenyl units linked to one phosphorus atom.

EXPERIMENTAL

Apparatus and Chemicals

Reactions with air-sensitive compounds were performed under argon using Schlenk techniques. ^{1}H (250 MHz), ^{13}C (63 MHz) and ^{31}P (101 MHz) NMR spectra were recorded with a Bruker 250 MHz spectrometer in $CDCl_3$. Chemical shifts are measured in ppm relative to internal TMS (for ^{1}H and ^{13}C spectra) and H_3PO_4 (for ^{31}P spectra). Flash column chromatography was performed on silica gel 60 (230–400 mesh) Merck. Mass spectrometry was performed on a Riber Mag R10-R10 with electronic ionisation or chemical desorption (NH_3). The solvents were freshly distilled and used dried. Butyl lithium (1.6 M) was obtained from Acros Chemicals and titrated before use against *N*-pivaloyl-*o*-toluidine[10] (**19**), (*S*,*S*)-(–)-2,3-*O*-isopropylidenethreitol 1,4-ditosylate (**19**), (*S*)-methyloxirane (**26**), diphenylphosphine and dicyclohexylphosphine were purchased from Aldrich.

Phenyl Diferrocenylphosphinite–Borane (**11**)

Tributylstannylferrocene **8** (4.75 g, 10 mmol), prepared according to ref.[7], was dissolved in 25 ml THF under argon at –78 °C. BuLi (7 ml of 1.5 M solution in hexane, 10.5 mmol) was added dropwise over 12 min. A red precipitate was formed. After stirring 30 min at –78 °C the transmetallation was complete. $P(OPh)_3$ (1.3 ml, 5 mmol) was added dropwise in 12 min. The precipitate was dissolved after 25 min stirring at –78 °C. Phosphinite **9** formed *in situ* was then protected as the borane adduct. Then BH_3·THF (10 ml of 1 M solution in THF, 10 mmol) was added in 2 min. The reaction mixture was stirred for 1 h at room temperature. Hydrolysis was performed by slow addition of 1 ml acetone at 0 °C followed after 10 min by 20 ml aqueous 2 M NaOH. An ether extraction yielded 6.1 g of crude product which was crystallized from a solvent mixture of 75 ml heptane and 15 ml toluene to give 1.7 g of

orange crystals (68%); m.p. 189–191 °C. For $C_{26}H_{26}BFe_2OP$ (508.0) calculated: 61.48% C, 5.16% H, 6.10% P; found: 61.35% C, 5.13% H, 6.32% P. ^{1}H NMR: 7.37–6.95 (m, 5 H, Ph); 4.60 (m, 2 H, subst.Cp); 4.53 (m, 2 H, subst.Cp); 4.48 (m, 4 H, subst.Cp); 4.21 (10 H, Cp); 1.7–1.3 (m, 3 H, BH_3). ^{13}C NMR: 152.1 (1 C, Ph); 129.1 (1 C, Ph); 124.1 (d, J_{PC} = 1.8, 2 C, Ph); 121.5 (d, J_{PC} = 3.7, 2 C, Ph); 72.5, 72.1, 71.8, 71.7, 71.6, 71.5, 71.3 (8 C, subst.Cp); 70.0 (10 C, Cp); 69.5 (1 C, subst.Cp); 66.1 (1 C, subst.Cp). MS, % (CI/NH_3): 526 (100, M + NH_4^+); 509 (15, M + H^+); 495 (28, M + H^+ – BH_3); 401 (49, M + H^+ – BH_3 – OPh); 187 (19, FcH + H^+).

Diferrocenylphosphine Oxide (**13**)

Tributylstannylferrocene **8** (19 g, 40 mmol) in 100 ml THF was treated under argon at –78 °C with BuLi (30 ml of 1.6 M solution in hexane, 48 mmol) over 30 min. After stirring for 50 min at –78 °C, $P(OPh)_3$ (4.75 ml, 18 mmol) was added in 5 min. After stirring for 50 min, hydrolysis was performed by an aqueous solution of 2 M HCl, with stirring at room temperature for 1 h. Extraction by dichloromethane and washing by 2 M NaOH and then by a saturated solution of NaCl gave a crude product. A column chromatography on deactivated alumina (elution by AcOEt–CH_2Cl_2, 90 : 10) removed Bu_4Sn and ferrocene, then the phosphorus compounds were recovered (elution by AcOEt–CH_2Cl_2, 75 : 25). A second column chromatography on deactivated alumina with elution by CH_2Cl_2 gave 1.5 g of triferrocenylphosphine (14%) followed by 5.0 g of pure **13** (60%); yellow crystals; m.p. 195–200 °C. For $C_{20}H_{19}Fe_2OP$ (418.1) calculated: 57.46% C, 4.58% H, 7.41% P; found: 57.21% C, 4.44% H, 7.71% P. ^{1}H NMR: 7.95 (d, $^1J_{PH}$ = 486, 1 H, PH); 4.41 (m, 2 H, subst.Cp); 4.43 (m, 6 H, subst.Cp); 4.30 (s, 10 H, Cp). ^{13}C NMR: 73.0, 71.6, 71.4, 71.3, 70.8, 70.3, 70.0 (10 C, subst.Cp); 69.5 (10 C, Cp). MS, % (EI, 70 eV): 418 (100, M^+); 232 (11, M – Fc – H); 186 (45, FcH); 121 (14, FeCp).

Diferrocenylphosphine–Borane (**12**)

Two methods can be used to prepare **12**. In the first approach **11** was reduced by $LiAlH_4$ into **12**. The other route, described below, involves the reduction of diferrocenylphosphine oxide **13** by the combination $LiAlH_4$–$CeCl_3$ (ref.[8]) followed by the addition of BH_3. Diferrocenylphosphine oxide **13** (2.1 g, 5 mmol) was added at 0 °C as a solid to a white suspension of $CeCl_3$ (15 mmol, dried for 3 h at 150 °C under vacuum in a Schlenk tube) in 25 ml THF and stirred 30 min under argon and cooled to 0 °C. After stirring for 90 min at room temperature and cooling to 0 °C BH_3·THF (20 ml of 1 M solution in THF, 20 mmol) was added. Hydrolysis was cautiously done by dropwise pouring onto a mixture of crushed ice (200 ml) and 20 ml of 12 M HCl. After a vigorous stirring the product was extracted into ethyl acetate and washed successively with 1 M HCl, saturated solution of NaCl and water. Solvents were evaporated under controled temperature (<40 °C) and the residue was dried 48 h under vacuum. Yield 1.8 g (88%); orange microcrystals; m.p. 161–166 °C. For $C_{20}H_{22}BFe_2P$ (415.9) calculated: 57.76% C, 5.34% H, 7.45% P; found: 57.72% C, 5.26% H, 6.16% P. ^{1}H NMR: 6.13 (qd, $^1J_{PH}$ = 382, $^3J_{HBPH}$ = 6.4, 1 H, PH); 4.45 (m, 6 H, subst.Cp); 4.42 (m, 2 H, subst.Cp); 4.21 (s, 10 H, Cp); 1.8–1.2 (m, 3 H, BH_3). ^{13}C NMR: 72.4 (2 C, subst.Cp); 72.2 (2 C, subst.Cp); 71.6 (d, J_{PC} = 6.9, 2 C, subst.Cp); 71.3 (d, J_{PC} = 8.1, 2 C, Ph); 72.5, 72.1, 71.8, 71.7, 71.6, 71.5, 71.3 (8 C, subst.Cp); 70.0 (10 C, Cp); 69.5 (2 C, subst.Cp); 69.6 (10 C, Cp); 65.9 (d, $1J_{PC}$ = 68, 2 C, subst.Cp). ^{13}P NMR: –16.2 (md, $^1J_{BP}$ = 51, 1 P). MS, % (CID/NH_3): 434 (24, M + NH_4^+); 417 (28, M + H^+); 403 (56, M + H^+ – BH_3); 219 (38, FcPH + H^+); 187 (100, FcH + H^+).

Diferrocenylphosphine (**1**)

DABCO (560 mg, 5 mmol) was added to phosphine–borane **12** (625 mg, 1.5 mmol) dissolved in 30 ml toluene under argon at room temperature. After heating at 60 °C for 4 h, the solution was cooled down to room temperature, filtered through a small column (deactivated alumina, ether) using a weak vacuum. Solvent evaporation left 595 mg of pure **1** (98%) as an orange solid; m.p. 137–138 °C. For $C_{20}H_{19}Fe_2P$ (402.1) calculated: 59.75% C, 4.77% H, 7.70% P; found: 59.51% C, 4.63% H, 7.91% P. ^{1}H NMR: 4.93 (d, $^1J_{PH}$ = 224.3, 1 H, PH); 4.27 (m, 2 H, subst.Cp); 4.23 (m, 6 H, subst.Cp); 4.13 (s, 10 H, Cp). ^{13}C NMR: 74.4, 74.9, 74.2, 73.9, 72.6, 70.6, 70.5, 70.4 (10 C, subst.Cp); 68.9 (10 C, Cp). ^{31}P NMR: –78.4 (s, 1 P). MS, % (EI, 70 eV): 402 (50, M^+); 216 (100, FcP).

(2*R*,3*R*)-4,5-Bis[(diferrocenylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane–Bis(borane) (**16**)

Compound **12** (873 mg, 2.1 mmol) was dissolved in 10 ml THF and cooled to –78 °C. BuLi in hexane (2.12 mmol) was added dropwise over 5 min and the mixture was stirred for 10 min at –78 °C. After heating to room temperature (10 min) and subsequent cooling to –78 °C, **19** (470 mg, 1 mmol), dissolved in 5 ml DMF, was added dropwise. After standing for 9 h and quenching with water the product was extracted with ether. The crude material was purified by column chromatography (alumina, dichloromethane–hexane, 1 : 1) giving **16** (850 mg, 82%) as a red-orange solid; m.p. 270–275 °C (decomp); $[\alpha]_D^{20}$ –24.5 (*c* 0.6, $CHCl_3$). For $C_{47}H_{54}B_2Fe_4O_2P_2$ (958.0) calculated: 58.93% C, 5.69% H, 2.26% B, 6.47% P; found: 58.91% C, 5.74% H, 2.02% B, 6.13% P. ^{1}H NMR: 4.52 (m, 4 H, subst.Cp); 4.47 (m, 2 H, subst.Cp); 4.45 (m, 4 H, subst.Cp); 4.39 (m, 2 H, subst.Cp); 4.33 (m, 2 H, subst.Cp); 4.20 (s + m, 10 H + 2 H, Cp + subst.Cp); 4.14 (s, 10 H, Cp); 3.67 (m, 2 H, OCH); 2.15 (m, 4 H, CH_2); 1.22 (s, CH, CH_3). ^{13}C NMR: 108.8 (1 C, OCO); 77.2 (2 C, subst.Cp); 72.6–70.6 (m, 18 C, subst.Cp); 69.4 (2 C, CO); 68.8 (20 C, Cp); 31.5 (d, $^1J_{PC}$ = 40, 2 C, P-CH_2); 27.0 (2 C, CH_3). MS, % (EI, 70 eV): 958 (23, M^+); 944 (100, M – BH_3); 930 (45, M – 2 BH_3); 745 (11, M – 2 BH_3 – Fc); 529 (1 M – 2 BH_3 – PFc_2); 465 (38, M – 2 BH_3 – PFc_2 – Cp); 400 (55, M – 2 BH_3 – 2 PFc_2 – Cp); 186 (17, FcH).

(2*R*,3*R*)-4,5-Bis[(diferrocenylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane (**17**)

A solution of **16** (195 mg , 2 mmol) and DABCO (225 mg, 2 mmol) in 15 ml toluene was stirred under argon for 4 h at 60 °C. The solution was filtered through a small column of deactivated alumina (elution with ether using a weak vacuum). After solvent evaporation pure **17** was obtained (quantitative yield) as an orange solid; m.p. 163–165 °C; $[\alpha]_D^{20}$ –115.8 (*c* 0.19, $CHCl_3$). For $C_{47}H_{48}Fe_4O_2P_2$ (930.3) calculated: 60.68% C, 5.20% H, 6.66% P; found: 60.85% C, 5.39% H, 6.75% P. ^{1}H NMR: 4.32 (m, 6 H, Cp + subst.Cp); 4.29 (m, 6 H, subst.Cp); 4.27 (m, 2 H, subst.Cp); 4.19 (s + m, 10 H + 2 H, subst.Cp); 4.17 (s + m, 10 H + 2 H, Cp + subst.Cp); 3.88 (m, 2 H, OCH); 2.34 (m, 1 H, subst.Cp); 2.19 (m, 2 H, PCH); 1.51 (s, 6 H, CH_3). ^{13}C NMR: 108.3 (1 C, OCO); 80.0, 79.8, 78.1, 72.7, 72.0, 71.0, 70.8, 69.9 (8 d, 20 C, subst.Cp); 69.8 (2 C, CO); 68.8 (20 C, Cp); 33.4 (d, 2 C, PCH_2); 21.3 (2 C, C-CH_3). ^{31}P NMR: –45.2 (s, 1 P). MS, %: 930 (19, M^+); 401 (100, Fc_2P); 216 (26, Fcp); 186 (80, FcH).

(2*R*,3*S*)-4[(Diferrocenylphosphino)methyl]-2,2-dimethyl-5-[(tosyloxy)methyl]-1,3-dioxolane–Borane (**20**)

Compound **12** (208 mg, 0.5 mmol) dissolved in 2 ml THF under argon was added dropwise to a suspension of *t*-BuOK (62 mg, 0.55 mmol) in 2 ml THF at 0 °C. After stirring 30 min at room temperature the precipitate disappeared, giving an orange solution. After cooling to 0 °C, a solution of **19** (235 mg, 0.5 mmol) in 2 ml THF was added dropwise. After stirring at room temperature for 2.5 h, an ether extraction and a flash chromatography (silica gel, hexane–AcOEt, 90 : 10) gave 50 mg of diphosphine **16** (10%) followed by pure phosphine **20** (170 mg, 48%) as an orange solid; m.p. 49–51 °C; $[\alpha]_D^{20}$ –14.0 (*c* 0.22, $CHCl_3$). For $C_{34}H_{40}BFe_2O_5PS$ (714.3) calculated: 57.18% C, 5.65% H, 4.34% P, 4.49% S; found: 57.02% C, 5.52% H, 4.26% P, 4.79% S. ^{1}H NMR: 7.76 (m, 2 H, Tol); 7.34 (m, 2 H, Tol); 4.53 (m, 1 H, subst.Cp); 4.49 (m, 1 H, subst.Cp); 4.45 (m, 3 H, subst.Cp); 4.39 (m, 1 H, subst.Cp); 4.34 (m, 1 H, subst.Cp); 4.21 (s + m, 5 H + 1 H, Cp + subst.Cp); 4.15 (s, 5 H, Cp); 4.15–3.8 (m, 4 H, OCH + $TsOCH_2$); 2.43 (s, 3 H, $ArCH_3$); 1.31 (s, 3 H, CH_3); 1.19 (s, 3 H, CH_3). ^{13}C NMR: 146.5 (1 C, Tol); 144.9 (1 C, Tol); 129.8 (2 C, Tol); 127.8 (2 C, Tol); 73.7, 68.6 (m, subst.Cp + CO); 69.4 (10 C, Cp); 29.5 (1 C, Ar-CH_3); 26.9 (d, $^1J_{PC}$ = 41.5, 1 C, P-CH_2); 21.5 (1 C, C-CH_3). ^{31}P NMR: 7.8 (m, 1 P). MS, % (CI/NH_3): 733 (100, M + NH_4^+); 714 (11, M^+); 702 (26, M + H^+ – BH_3); 186 (67, FcH).

(2*R*,3*S*)-4-[(Diferrocenylphosphino)methyl]-2,2-dimethyl-5-[(tosyloxy)methyl]-1,3-dioxolane (**21**)

DABCO (400 mg, 3.5 mmol) and **20** (500 mg, 0.7 mmol) were dissolved in toluene and heated for 5 h. The reaction mixture was dissolved in ethyl acetate, filtered through alumina and evaporated to dryness. After 9 h, it was quenched with water, extracted with ether and evaporated to dryness. Subsequent evaporation of the solvent gave quantitatively **21** as an orange solid. For $C_{34}H_{37}Fe_2O_5PS$ (700.4) calculated: 58.31% C, 5.32% H, 4.42% P; found: 58.84% C, 5.61% H, 4.25% P. ^{1}H NMR: 7.80 (d, 2 H); 7.35 (m, 2 H); 4.40–3.90 (m); 2.95 (q); 2.79 (s); 2.20 (m); 2.05 (s); 1.68 (s); 1.44 (s); 1. 33 (s); 1.25 (t). ^{31}P NMR: –45.9 (s).

(2*R*,3*R*)-4-[(Dicyclohexylphosphino)methyl]-5-[(diferrocenylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane–Bis(borane) (**22**)

Dicyclohexylphosphine–borane was prepared from dicyclohexylphosphine and $BH_3{\cdot}SMe_2$ in ether at 0 °C and then 2 h at room temperature. After filtration through alumina under argon and evaporation to dryness it gave quantitatively a solid adduct (^{31}P NMR: 18.2 (q)) which was used without further purification. Dicyclohexylphosphine–borane (429 mg, 2.02 mmol) dissolved in 10 ml THF was cooled to –78 °C. BuLi in hexane (2.02 mmol) was added in 5 min and the mixture stirred for 10 min followed by stirring for 10 min at room temperature. After re-cooling to –78 °C, tosylate **20** (1.18 g, 2.02 mmol) dissolved in 5 ml DMF was introduced. The mixture was left standing overnight, quenched with water and extracted with ether. Recrystallization from ethyl acetate–pentane afforded 882 mg (68%) of **22** as orange needles; m.p. 181–182 °C; $[\alpha]_D^{20}$ –12.1 (*c* 1.00, $CHCl_3$). For $C_{39}H_{58}B_2Fe_2O_2P_2$ (754.2) calculated: 62.11% C, 7.75% H, 8.21% P; found: 62.15% C, 7.88% H, 8.24% P. ^{1}H NMR: 4.28 (s, Cp); 4.18 (s, Cp); 2.35 (m, 2 H); 1.57 (s); 1.32 (s); 1.28 (s). ^{31}P NMR: 26.34; 9.13. MS, %: 726 (M^+); 643; 481; 217; 186.

(2*R*,3*S*)-4-[(Diferrocenylphosphino)methyl]-5-[(diphenylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane–Bis(borane) (**23**)

Diphenylphosphine–borane (383 mg, 1.91 mmol) in 30 ml THF was cooled to –78 °C. BuLi in hexane (2. 10 mmol) was added and the mixture stirred for 10 min at –78 °C. After keeping at room temperature (10 min) and subsequent cooling to –78 °C, tosylate **20** (1.24 g, 1.74 mmol) dissolved in 10 ml DMF was introduced. Quenching with water (after overnight stay) and extraction with ether and crystallization from ethyl acetate–hexane afforded **23** as orange needles (967 mg, 75%); m.p. 195–196 °C; $[\alpha]_D^{20}$ –83.7 (*c* 0.08, $CHCl_3$). For $C_{39}H_{52}B_2Fe_2O_2P_2$ (748.0) calculated: 62.62% C, 7.01% H, 8.28% P; found: 61.33% C, 6.02% H, 7.33% P. ^{1}H NMR: 7.25–7.80 (m, Ar); 4.25–4.60 (m); 4.18 (s); 4.20 (s); 1.10 (s, Me); 1.05 (s, Me). ^{13}C NMR: 133.4–128.9 (9 peaks); 78.04–70.1 (19 peaks); 128.0–130.0 (4 peaks); 32.7; 32.2; 30.0; 27.7; 29.5; 27.7; 27.5. ^{31}P NMR: 15.42; 8.31. MS, %: 748 (M^+); 529; 401; 213; 185.

(2*R*,3*S*)-4-[(Diferrocenylphosphino)methyl]-5-[(diphenylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane (**24**)

Borane **23** (238 mg, 0.32 mmol) was refluxed in diethylamine under argon overnight. After evaporation to dryness the crude product was chromatographed on silica (pentane–ethyl acetate, 9 : 1). The title product **24** was isolated in 80% yield; $[\alpha]_D^{20}$ –39.0 (*c* 0.10, $CHCl_3$). ^{1}H NMR: 7.30–7.50 (m, 10 H, Ph); 4.6–4.0 (m, 8 H, subst.Cp); 4.25 (s, 5 H, Cp); 4.12 (s, 5 H, Cp); 3.90 (q, 1 H); 3.62 (q, 1 H); 2.50 (dt, 1 H); 2.10–2.40 (m, 2 H); 1.15 (2 s, 2 CH_3). ^{13}C NMR: 138.0 (2 peaks); 135.3 (3 peaks); 128.0–130.0 (4 peaks); 109.0; 74.0–69.0 (14 peaks); 61.0; 30.4–30.2 (4 peaks); 30.0; 27.7; 27.5; 21.8; 19.6. ^{31}P NMR: 7.8 (m, 1 P). MS, % (CI/NH_3): 728 (10); 716 (22); 714 (60); 529 (65); 401 (100); 368 (52); 353 (10); 334 (10).

(2*R*,3*R*)-4-[(Dicyclohexylphosphino)methyl]-5-[(diferrocenylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane (**25**)

A solution of **22** (200 mg, 0.27 mmol) in diethylamine was refluxed under argon overnight. After evaporation to dryness and column chromatography under argon (ethyl acetate–pentane, 1 : 4), **25** was isolated in 85% yield as a yellow solid; m.p. 44–46 °C; $[\alpha]_D^{20}$ –104.8 (*c* 1.0, $CHCl_3$). For $C_{39}H_{52}Fe_2O_2P_2$ (726.5) calculated: 64.48% C, 7.21% H, 8.49% P; found: 63.85% C, 7.62% H, 9.04% P. ^{1}H NMR: 4.35–4.25 (m); 4.20 (s, Cp); 4.15 (s, Cp); 4.05 (s); 3.80 (broad); 2.54 (d); 2.15 (m); 1.75 (m); 1.60 (s); 1.45 (d); 1.20 (broad). ^{13}C NMR: 108.1; 79.8; 77.5; 77.0; 76.5; 73.5; 73.1; 70.6; 70.0–66.6 (7 peaks); 33.7–33.0 (10 peaks). ^{31}P NMR: –13.93 (s); –44.51 (s).

(*S*)-1-(Diferrocenylphosphino)propan-2-ol–Borane (**27**)

Diferrocenylphosphine–borane (**12**) (1.50 g, 3.6 mmol) dissolved in THF was cooled to –78 °C. To this solution BuLi in hexane (4.0 mmol) was added. Following a stirring for 30 min at –78 °C the solution was allowed to warm up to room temperature. After cooling again at –78 °C (*S*)-propylene oxide (3.6 mmol) was added dropwise and the solution was left overnight. Quenching with water and ether extraction gave the crude product which was purified by column chromatography (silica), affording **27** (1.53 g, 90%). ^{1}H NMR: 4.5–4.0 (m, subst.Cp); 4.28 (s, 10 H, Cp); 4.16 (s, 10 H, Cp); 2.85 (s, OH); 2.25 (m, 3 H); 1.24 (dd, J = 6, J = 1.3,

3 H, Me). ^{13}C NMR: 72.3; 72.1; 72.0; 71.8; 71.4; 71.3; 71.2; 71.1; 71.0; 70.9; 70.7; 70.4; 69.75; 69.72; 69.5; 66.2; 63.5; 39.2; 38.6; 24.9; 24.7.

(*S*)-1-(Diferrocenylphosphino)-2-(tosyloxy)propane–Borane (**28**)

Alcohol **27** (903 mg, 1.90 mmol), 4-dimethylaminopyridine (DMAP) (464 mg, 3.8 mmol) and tosyl chloride (726 mg, 3.8 mmol) were refluxed in dichloromethane for 4 h. The solution was filtered on silica, which was washed by some dichloromethane. Solvent evaporation and crystallization from a heptane–chloroform mixture gave **28** (800 mg, 81%); m.p. 148–150 °C (dec); $[\alpha]_D^{20}$ –92.0. (*c* 0.20, $CHCl_3$). ^{1}H NMR: 7.70 (d, Ar); 7.30 (m, Ar); 4.30–4.70 (subst.Cp); 4.15 (2 s, 10 H, 2 Cp); 2.80 (t, 1 H); 2.42 (s, 3 H, Me tolyl); 2.40 (m, 2 H); 0.6–1.8 (broad, BH_3); 1.15 (d, Me). ^{13}C NMR: 145.3; 134.1; 130.4; 128.4; 78.0; 77.8; 77.5; 77.3; 77.1; 72.5; 72.4; 72.37; 72.31; 72.1; 72.0; 71.9; 71.8; 71.7; 71.6; 71.0; 70.7; 69.5; 70.36; 70.32; 37.3; 36.8; 24.9; 22.7; 22.2.

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REFERENCES

1. Hayashi T., Kumada M.: *Acc. Chem. Res.* **1982**, *15*, 395.
2. Kagan H. B., Sasaki M. in: *The Chemistry of Organophosphorus Compounds* (F. R. Hartley, Ed.), Vol. 1, Chap. 3. J. Wiley and Sons, New York 1990.
3. Hayashi T. in: *Ferrocenes* (T. Hayashi and A. Togni, Eds), Chap. 2. VCH, Weinheim 1995.
4. Brunner H., Zettlmeier W.: *Handbook of Enantioselective Catalysis with Transition Metal Compounds*, Volumes I and II. VCH, Weinheim 1993.
5. Perea J. J. A., Lotz M., Knochel P.: *Tetrahedron: Asymmetry* **1999**, *10*, 375; and references therein.
6. a) Sollot G. P., Peterson W. R. J. J.: *J. Organomet. Chem.* **1969**, *19*, 143; b) Nesmeyanov M. N., Vilchevskaya V. D., Krylova A. I., Nekrasov Y. S., Tolkunova V. S.: *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* **1975**, 635.
7. Guillaneux D., Kagan H. B.: *J. Org. Chem.* **1995**, *60*, 2502.
8. Imamoto T., Oshiki T., Onozawa T., Kusumoto T., Sato K.: *J. Am. Chem. Soc.* **1990**, *112*, 5244.
9. a) Dang T. P., Kagan H. B.: *J. Chem. Soc., Chem. Commun.* **1971**, 481; b) Dang T. P., Kagan H. B.: *J. Am. Chem. Soc.* **1992**, *94*, 6429.
10. Suffert J.: *J. Org. Chem.* **1989**, *54*, 509.