Synthesis of Josiphos-Type Bisphospholane Ligands

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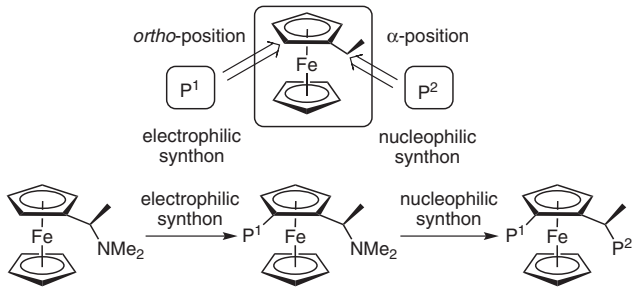
Abstract: Bisphospholane Josiphos-type ligands were synthesized in high yields employing electrophilic and nucleophilic phospholane synthons. Full characterization data including solid-state structures of the diastereomeric ligands are reported. These ligands resulted in active and enantioselective iridium catalysts for the asymmetric hydrogenation of imines. Pronounced cooperative effects of the chiral elements within the ligand structure were observed and enantioselectivities of up to 74% ee were achieved.

Key words: ferrocene ligands, chiral phospholane, asymmetric hydrogenation, iridium, imine hydrogenation

In 1994, Togni[2] developed an efficient and modular approach for the synthesis of ferrocene-based bidentate phosphorous ligands (Josiphos-type) elaborating a procedure of Kumada and Hayashi.[3] Josiphos-type bisphosphines are extremely useful ligands for asymmetric catalysis and have been applied up to now in four different industrial processes including the large-scale production of (*S*)-Metolachlor.[4]

The Josiphos ligands are available via a two-step synthesis starting from enantiomerically pure Ugi's amine.[5] Due to the consecutive introduction of the phosphorus moieties, the synthesis is quite flexible and allows for functionalization with two different donor groups.



Scheme 1 Togni's ferrocene 'construction kit'[2b]

In the first step an electrophilic synthon is introduced in the *ortho* position of Ugi's amine, while in the second step the dimethylamino group is substituted by a nucleophilic phosphine synthon. This synthetic approach, known as 'Togni's ferrocene construction kit' (Scheme 1),[2b] has been successfully used for the synthesis of numerous of ligand structures.[6]

Following this reaction sequence, in 2004 Salzer and co-workers[7] reported the first example of a Josiphos derivative bearing a phospholane moiety in the side chain (α-position). The resulting hybrid phosphine-phospholane ligand led to excellent results in the asymmetric hydrogenation of dimethyl itaconate with >99% ee. Recently, Börner and co-workers introduced a phospholane unit in the *ortho* position of Ugi's amine through an electrophilic phospholane synthon resulting in a bidentate *P*,*N*-ligand.[8]

Intrigued by the possibility to integrate the privileged structural motifs of the Josiphos backbone, based on planar and central chirality, with two chiral phospholane units, we sought to synthesize bisphospholane counterparts of the Josiphos bisphosphine ligands.

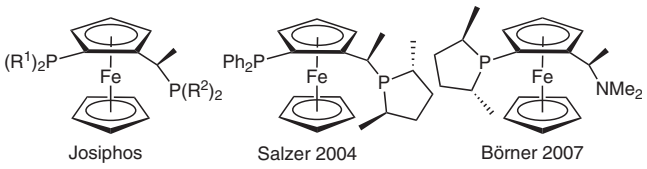
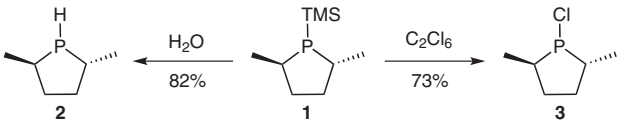


Figure 1 Josiphos and related derivatives

Both the nucleophilic synthons (2*R*,5*R*)-2,5-dimethylphospholane (**2**) and the electrophilic synthon (*R*,*R*)-1-chloro-2,5-dimethylphospholane (**3**)[9] could be conveniently obtained from (*R*,*R*)-2,5-dimethyl-1-(trimethylsilyl)phospholane (**1**) in a one-step procedure (Scheme 2). By treating **1** with either an excess of degassed water or methanol, quantitative conversion into the corresponding secondary phospholane was achieved.[10] After distillation (bp 132–133 °C), analytically pure secondary phospholane **2** was obtained as colorless oil in 82% yield. Chlorophospholane **3** was synthesized from **1** via an umpolung reaction with hexachloroethane (yield: 73%).[8] Both transformations were carried out using enantiomerically pure (*R*,*R*)-2,5-dimethyl-1-(trimethylsilyl)phospholane (**1**) as the starting material and proceeded without loss of optical purity.



Scheme 2 Synthesis of the nucleophilic and electrophilic phospholane synthons **2** and **3**, respectively

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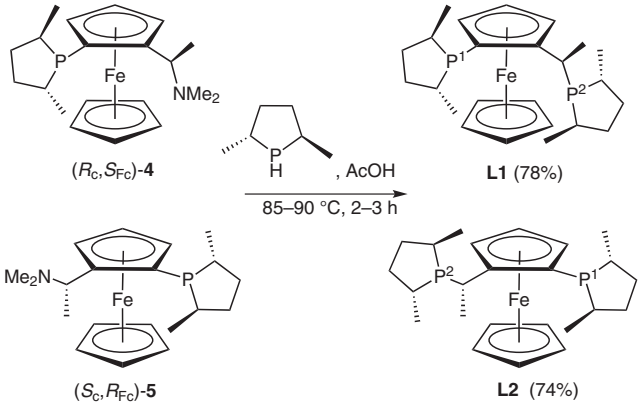
Ligand precursors (R_C,S_{Fc})-**4** and (S_C,R_{Fc})-**4** were synthesized via the route published by Börner.[8] The synthesis is straightforward and pure products (R_C,S_{Fc})-**4** and (S_C,R_{Fc})-**4** were obtained after recrystallization from hot methanol in 81% and 83% yield, respectively. For the introduction of the phospholane moiety into the side chain of the ligand precursors (Scheme 3), the standard method was adapted.[2a] The precursors (R_C,S_{Fc})-**4** and (S_C,R_{Fc})-**4** were refluxed in glacial acetic acid together with secondary phospholane **2** leading to the desired bisphospholanes **L1** and **L2**, respectively, in good yields after recrystallization from hot ethanol (**L1**, 78%; **L2**, 74%). Single crystals suitable for X-ray diffractometric analysis were obtained from cold ethanol and the molecular structures of **L1** and **L2** in the solid state were determined.



Scheme 3 Synthesis of ligand **L1** and **L2**

In the solid state structure of **L1** the two phosphorus atoms are quite far apart (5.272 Å) and their lone pairs have an almost antiperiplanar orientation (Figure 2). This arrangement is unusual for Josiphos-type ligands as confirmed by the torsion angles α1(C11–C1–P1–C2) of –106.03° and α2(C9–C8–C12–C19) of –73.20°, which are well beyond the range of values typically found for free (R_C,S_{Fc})-Josiphos derivatives (α1 = –60° to –82°; α2 = –10° to –32°).[11] In contrast, the two phosphorus atoms in the solid state structure of (S_C,R_{Fc})-**L2** (Figure 3) are much closer (3.803 Å), the lone pairs are almost synperiplanar, and the torsion angles α1(C17–C16–P2–C12) (+58.83°) and α2(C19–C15–C7–C8) (+30.35°) in line with the values measured for other (R_C,S_{Fc})-Josiphos ligands, upon inverting the sign because of the opposite chirality at the ferrocene backbone. The arrangement of the cyclopentadienyl rings in **L1** is almost staggered (25.76°), whereas in **L2** is nearly eclipsed (6.31°). Selected crystallographic data, bond lengths and angles for **L1** and **L2** are summarized in Tables 1–3.

The ^{31}P NMR of **L1** shows two singlets, at δ = –2.0 and +24.1 arising from the phospholanes in the *ortho* position and in the α-position, respectively. In contrast, the ^{31}P NMR spectrum of **L2** shows two doublets, at δ = –11.6 and 16.6 for the phospholane in the *ortho* position and the α-phospholane, respectively, with a coupling constant of

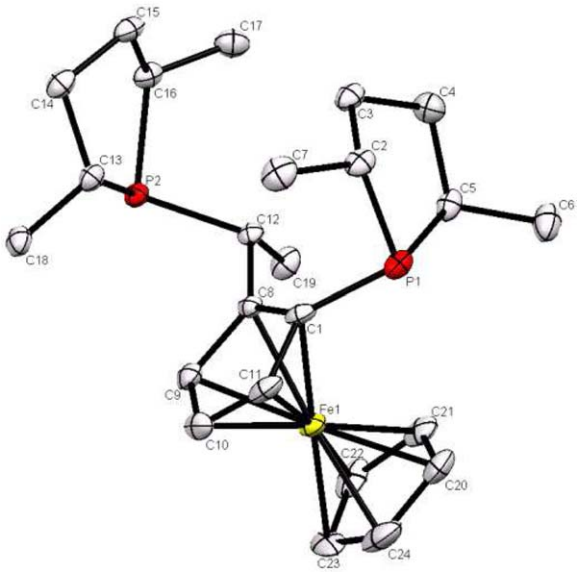


Figure 2 ORTEP representation of **L1** (50% probability, hydrogen atoms omitted for clarity)

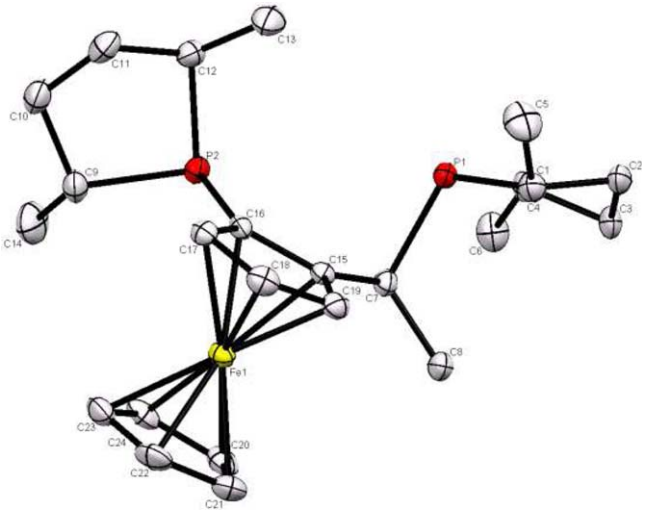


Figure 3 ORTEP representation of **L2** (50% probability, hydrogen atoms omitted for clarity)

Table 1 Comparison of Principal Crystallographic Data of **L1** and **L2**

Ligand	**L1**	**L2**
crystal system	monoclinic	orthorhombic
space group	$P2_1$	$P2_12_12_1$
P^1,P^2 distance	5.272 Å	3.803 Å
dihedral angle Cp–Cp′	25.76°	6.31°

Table 2 Selected Distances and Angles for **L1**

Distances (Å)		Angles (°)	
P1–C1	1.820(4)	C1–P1–C2	104.40(1)
P1–C2	1.861(3)	C2–P1–C5	92.70(1)
P1–C5	1.872(3)	C1–P1–C5	105.30(1)
P2–C12	1.882(3)	C12–P2–C16	104.67(1)
P2–C13	1.882(3)	C16–P2–C13	92.98(1)
P2–C16	1.879(3)	C12–P2–C13	104.54(1)
		α1(C11–C1–P1–C2)	–106.03
		α2(C9–C8–C12–C19)	–73.20

Table 3 Selected Distances and Angles for **L2**

Distances (Å)		Angles (°)	
P2–C16	1.831(3)	C16–P2–C12	101.64(1)
P2–C9	1.887(3)	C9–P2–C12	92.43(1)
P2–C12	1.887(3)	C9–P2–C16	102.02(1)
P1–C7	1.879(3)	C1–P1–C7	106.06(1)
P1–C4	1.874(3)	C1–P1–C4	92.78(1)
P1–C1	1.865(3)	C4–P1–C7	103.00(1)
		α1(C17–C16–P2–C12)	+58.83
		α2(C19–C15–C7–C8)	+30.35

$J_{P1,P2}$ = 23.3 Hz (Table 4). As the presence and magnitude of through space coupling constant between two phosphorus atoms depends on their distance and the relative orientation of their lone pairs,[12] the preferential conformation in solution of the phospholane groups in **L1** and in **L2** should be significantly different, far apart in **L1** and close to each other in **L2**.[13] This qualitative assumption correlates very well with the arrangements found in the solid-state structure of **L1** (Figure 2) and **L2** (Figure 3).

Table 4 Selected Analytical Data for **L1** and **L2**

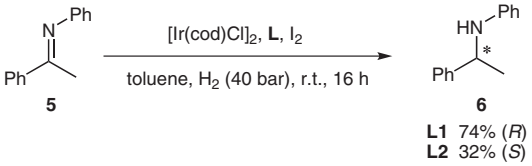
Ligand	^{31}P NMR (δ)			$[\alpha]_D^{24}$
	P^1	P^2	$J_{P1,P2}$ (Hz)	
L1	–2.0	+24.1	–	+71.63
L2	–11.6	+16.6	23.3	+266.8

To evaluate the σ-donor properties of the distinct phospholane groups of **L1** and **L2**, they were converted into the corresponding phospholane selenides by treating them with elemental selenium at 60 °C for two hours in benzene (Table 5). The coupling constant $J_{Se,P}$ is a suitable tool for classifying phosphorus ligands, whereby a smaller coupling constant reflects a higher P-basicity.[14] The ^{31}P–^{77}Se coupling constants for the bisselenides of **L1** and **L2** (Table 5) lie within the range reported for phospholane selenides (710–780 Hz).[15] The phosphorus atoms of **L1** and **L2** in the *ortho* position showed $J_{Se,P}$ = 713 and 718 Hz, respectively, similar to the value registered for the corresponding MeDuPhos derivative (712 Hz). The coupling constants of the phospholane selenides in the α-position are significantly higher (727 Hz for **L1** and 726 Hz for **L2**) and closer to the value reported for Se=PPh_3 (732 Hz).[14a]

Table 5 ^{31}P NMR Data of Selected *P*-Selenides

Selenide	^{31}P NMR			
	P^1 (δ)	$J_{Se,P1}$ (Hz)	P^2 (δ)	$J_{Se,P2}$ (Hz)
L1	+48.7	713	+74.0	727
L2	+53.4	718	+68.6	726
MeDuPhos	+61.0	712	–	–
PPh_3	+35.9	732	–	–

The diastereomeric ligands **L1** and **L2** were applied in the iridium-catalyzed asymmetric hydrogenation of *N*-(1-phenylethylidene)aniline (**5**) as a model substrate (Scheme 4).



Scheme 4 Iridium-catalyzed imine hydrogenation with **L1** and **L2**

Full conversion was obtained with both ligands. Ligand **L1** led to 74% ee in favor of the (*R*)-product, whereas **L2** led to the preferential formation of the opposite enantiomer with significantly lower enantioselectivity of 32% ee. These results indicate a pronounced cooperative effect of the chiral information from the ferrocene backbone and the chirality of phospholane moieties. For this particular reaction, ligand **L1** provides the matched diastereomer. Comparable effects have been observed by Togni[16] using P-chiral Josiphos diastereomers and by Zheng[13] with related phosphine-phosphoramidite ligands.

In conclusion, the first bisphospholane Josiphos-type ligands were synthesized. The ligands have been fully characterized both in solution and in the solid state via X-ray diffractometry. The coupling constants $J_{Se,P}$ of the corresponding bisselenides indicated, that the electronic features of these ligands resemble that of phosphine-phospholanes. Strong cooperative effects of the chiral elements within the ligand structure were observed in the

iridium-catalyzed asymmetric hydrogenation of an imine and enantioselectivities of up to 74% ee have been obtained with the matched diastereomer **L1**.

All reactions were carried out under an inert atmosphere of dry and O_2-free argon either with the use of standard Schlenk techniques or in a glove box. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with Bruker AV 300 spectrometer operating at 300.1 MHz (^{1}H), 75.5 MHz (^{13}C), and 121.5 MHz (^{31}P) and Bruker AV 400 spectrometer operating at 400.1 MHz (^{1}H), 100 MHz (^{13}C), and 162 MHz (^{31}P); ^{1}H and ^{13}C{^{1}H} NMR are relative to TMS with use of the residual solvent signals as internal standards and ^{31}P NMR are relative to 85% H_3PO_4 as external standard. The multiplicities of the signals were analyzed by assuming spectra of first order. The signals were assigned on the basis of 2D NMR spectra (^{31}P-^{1}H HMBC, ^{1}H-^{1}H COSY, ^{13}C-^{1}H HMBC, ^{13}C-^{1}H HSQC). Mass spectra were recorded on a Varian 1200L Quadrupole GC-MS, Finnigan MAT 8200 (MS and HRMS-EI) or a Bruker FTICR-Apex III spectrometer (HRMS-ESI). HRMS were performed with a Finnigan-MAT 95 spectrometer (EI, 70 eV). Optical rotations were measured on a Jasco P-1020 polarimeter. The concentrations used for measuring specific rotations are given as g/100 mL. Toluene was dried over alumina with a solvent purification system from Innovative Technology. Et_2O, MeOH, and EtOH were distilled and then dried over molecular sieves. All other organic solvents were purged with argon for 2 h prior to use. Deuterated solvents were degassed through freeze–pump–thaw cycles and stored over molecular sieves. Compounds **2**,[10] **3**,[8] and **4**[8] were synthesized according to literature procedures. All other chemicals were purchased from Sigma-Aldrich, Acros, or Alfa Aesar and used as received.

(S_{Fc})-2-[(*R*)-1-(Dimethylamino)ethyl]-1-[(2*R*,5*R*)-2,5-dimethylphospholan-1-yl]ferrocene {(R_C,S_{Fc})-[C_5H_5]Fe[C_5H_3(CHMeNMe$_2$){(*R*,*R*)-DMP}], (R_C,S_{Fc})-4**}[8]**

A 1.5 M *t*-BuLi in pentane soln (1.01 mL, 1.51 mmol) was added at –78 °C over 30 min through a syringe pump to a soln of (–)-(*R*)-*N*,*N*-dimethyl-1-ferrocenylethylamine (Ugi-amine, 312.2 mg, 1.21 mmol, 1.0 equiv) in Et_2O (10 mL). After stirring the soln at r.t. for 1 h, (2*R*,5*R*)-1-chloro-2,5-dimethylphospholane (**3**, 219.4 mg, 1.46 mmol, 1.2 equiv) was added and the resulting mixture heated to reflux for 2.5 h. The mixture was filtered through a short pad of Celite and the solvent removed under reduced pressure. The pure product was obtained as an orange solid after recrystallization (hot MeOH, 2 mL); yield: 356.4 mg (1.0 mmol, 81%).

^{1}H NMR (400 MHz, C_6D_6): δ = 1.13 (d, $J_{H,P}$ = 6.7 Hz, 3 H, CH_3), 1.21 (m, 1 H, CH_2), 1.37 (dd, $J_{H,H}$ = 7.1 Hz, $J_{H,P}$ = 18.9 Hz, 3 H, CH_3), 1.54 (dd, $J_{H,H}$ = 7.7 Hz, $J_{H,P}$ = 2.3 Hz, 3 H, CH_3), 1.74–1.87 (m, 1 H, CH_2), 1.88–2.01 (m, 1 H, CH_2), 2.10 (s, 6 H, 2 CH_3), 2.09–2.20 (br m, 3 H, CH, CH_2), 3.95 (br s, 1 H, CH_{Cp}), 3.90–4.05 (m, 6 H, CH_{Cp}), 4.08 (br s, 1 H, CH_{Cp}), 4.14–4.25 (m, 1 H, CH).

^{13}C NMR (101 MHz, C_6D_6): δ = 7.4 (CH_3), 16.1 (CH_3), 21.7 (d, $J_{C,P}$ = 30.8 Hz, CH_3), 36.1 (d, $J_{C,P}$ = 11.4 Hz, CH), 37.0 (d, $J_{C,P}$ = 3.8 Hz, CH_2), 38.2 (d, $J_{C,P}$ = 5.2 Hz, CH_2), 39.2 (2 CH_3), 41.6 (d, $J_{C,P}$ = 9.8 Hz, CH), 57.0 (d, $J_{C,P}$ = 8.7 Hz, CH), 67.9 (CH_{Cp}), 68.5 (CH_{Cp}), 70.2 (5 CH_{Cp}), 72.2 (d, $J_{C,P}$ = 4.7 Hz, CH_{Cp}), 79.4 (d, $J_{C,P}$ = 32.7 Hz, C_{Cp}), 96.1 (d, $J_{C,P}$ = 19.2 Hz, C_{Cp}).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ = –5.8.

(S_{Fc})-1-[(2*R*,5*R*)-2,5-Dimethylphospholan-1-yl]-2-{(*R*)-1-[(2*R*,5*R*)-2,5-dimethylphospholan-1-yl]ethyl}ferrocene {(R_C,S_{Fc})-[C_5H_5]Fe[C_5H_3(CHMe{(*R*,*R*)-DMP}){(*R*,*R*)-DMP}], L1}

(2*R*,5*R*)-2,5-Dimethylphospholane (117.6 mg, 1.01 mmol, 1 equiv) was added to a soln of (R_C,S_{Fc})-**4** (374.1 mg, 1.01 mmol, 1 equiv) in glacial AcOH (5 mL) and heated to reflux for 2 h. The solvent was removed in vacuo and the resulting solid was recrystallized (hot EtOH, 3 mL) to give the pure product as an orange solid; yield: 394.4 mg (0.79 mmol, 78%).

$[\alpha]_D^{24}$ +71.6 (*c* 0.393, CH_2Cl_2).

^{1}H NMR (400 MHz, C_6D_6): δ = 0.97–1.04 (m, 1 H, CH_2), 1.10 (dd, $J_{H,H}$ = 6.9 Hz, $J_{H,P}$ = 17.3 Hz, 3 H, CH_3), 1.16–1.25 (br m, 1 H, CH), 1.20 (t, $J_{H,H,P}$ = 7.1 Hz, 3 H, CH_3), 1.31 (dd, $J_{H,H}$ = 7.4 Hz, $J_{H,P}$ = 18.7 Hz, 3 H, CH_3), 1.42 (dd, $J_{H,H}$ = 7.3 Hz, $J_{H,P}$ = 10.4 Hz, 3 H, CH_3),1.47–1.61 (br m, 1 H, CH_2), 1.67–1.77 (br m, 1 H, CH_2), 1.69 (dd, $J_{H,H}$ = 7.0 Hz, $J_{H,P}$ = 15.1 Hz, 3 H, CH_3), 1.79–1.87 (m, 2 H, CH + CH_2), 1.90–2.06 (br m, 4 H, 2 CH + 2 CH_2), 2.09–2.17 (m, 1 H, CH_2), 2.37–2.52 (m, 1 H, CH_2), 2.92–3.02 (m, 1 H, CH), 3.88–3.96 (m, 1 H, $C_{Cp}H$), 3.99–4.08 (m, 1 H, $C_{Cp}H$), 4.12 (s, 5 H, $C_{Cp}H$), 4.42 (s, 1 H, $C_{Cp}H$).

^{13}C NMR (101 MHz, C_6D_6): δ = 15.6 (CH_3), 15.9 (CH_3), 21.6 (d, $J_{C,P}$ = 31.6 Hz, CH_3), 22.1 (d, $J_{C,P}$ = 31.0 Hz, CH_3), 25.0 (CH_3), 25.3 (CH), 34.1 (CH), 34.9 (d, $J_{C,P}$ = 12.7 Hz, CH), 35.8 (d, $J_{C,P}$ = 8.1 Hz, CH), 35.9 (CH_2), 36.8 (CH_2), 37.5 (CH_2), 38.1 (d, $J_{C,P}$ = 3.6 Hz, CH_2), 38.6 (CH), 68.5 ($C_{Cp}H$), 68.9 ($C_{Cp}H$), 69.9 (5 $C_{Cp}H$), 71.3 (d, $J_{C,P}$ = 4.6 Hz, $C_{Cp}H$); the quaternary C-atoms of the Cp rings could not be detected.

^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ = –2.0 (*o*-P), 24.1 (α-P).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{24}H_{36}FeP_2$: 442.16362; found: 442.16366.

(R_{Fc})-1-[(2*R*,5*R*)-2,5-Dimethylphospholan-1-yl]-2-{(*S*)-1-[(2*R*,5*R*)-2,5-dimethylphospholan-1-yl]ethyl}ferrocene {(S_C,R_{Fc})-[C_5H_5]Fe[C_5H_3(CHMe{(*R*,*R*)-DMP}){(*R*,*R*)-DMP}], L2}

The title compound was obtained as an orange solid starting from (S_C,R_{Fc})-**4** using the procedure described for **L1**; yield: 320.8 mg (0.73 mmol, 74%).

$[\alpha]_D^{24}$ +266.8 (*c* 0.393, CH_2Cl_2).

^{1}H NMR (400 MHz, C_6D_6): δ = 1.04 (m, 1 H, CH_2), 1.11 (dd, $J_{H,H}$ = 7.1 Hz, $J_{H,P}$ = 17.1 Hz, 3 H, CH_3), 1.16 (dd, $J_{H,H}$ = 7.2 Hz, $J_{H,P}$ = 9.1 Hz, 3 H, CH_3), 1.19–1.23 (br m, 1 H, CH), 1.26 (dd, $J_{H,H}$ = 7.4 Hz, $J_{H,P}$ = 8.7 Hz, 3 H, CH_3), 1.31–1.37 (m, 1 H, CH_2), 1.48 (dd, $J_{H,H}$ = 7.3 Hz, $J_{H,P}$ = 19.1 Hz, 3 H, CH_3), 1.49 (dd, $J_{H,H}$ = 4.4 Hz, $J_{H,P}$ = 7.0 Hz, 3 H, CH_3), 1.52–1.58 (br m, 1 H, CH_2), 1.76 (m, 1 H, CH_2), 1.85–1.97 (br m, 2 H, CH_2), 2.00–2.10 (br m, 2 H, CH_2), 2.10–2.19 (m, 1 H, CH), 2.20–2.37 (m, 1 H, CH), 2.59–2.73 (m, 1 H, CH), 3.39–3.49 (m, 1 H, CH), 3.84–3.92 (m, 1 H, $C_{Cp}H$), 4.06 (s, 1 H, $C_{Cp}H$), 4.07–4.14 (m, 1 H, $C_{Cp}H$), 4.12 (s, 5 H, $C_{Cp}H$).

^{13}C NMR (101 MHz, C_6D_6): δ = 14.7 (CH_3), 17.8 (d, $J_{C,P}$ = 14.7 Hz, CH_3), 18.7 (CH_3), 21.4 (d, $J_{C,P}$ = 33.0 Hz, CH_3), 22.6 (d, $J_{C,P}$ = 37.3 Hz, CH_3), 26.7 (CH), 30.7 (d, $J_{C,P}$ = 17.7 Hz, CH), 35.8 (d, $J_{C,P}$ = 11.8 Hz, CH), 36.1 (d, $J_{C,P}$ = 17.6 Hz, CH), 36.5 (CH_2), 36.8 (d, $J_{C,P}$ = 8.7 Hz, CH), 37.4 (CH_2), 37.6 (d, $J_{C,P}$ = 2.5 Hz, CH_2), 38.2 (d, $J_{C,P}$ = 3.8 Hz, CH_2), 68.0 ($C_{Cp}H$), 68.5 ($C_{Cp}H$), 69.2 (5 $C_{Cp}H$), 70.8 (d, $J_{C,P}$ = 6.4 Hz, CH_{Cp}), 75.7 (C_{Cp}), 102.1 (C_{Cp}).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ = –11.6 (d, $J_{P,P}$ = 23.3 Hz, *o*-P), 16.6 (d, $J_{P,P}$ = 23.3 Hz, α-P).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{24}H_{36}FeP_2$: 442.16362; found: 442.16338.

Selenide Formation; General Procedure

Bisselenides of **L1** and **L2** were prepared by treating a NMR sample of the bisphospholanes with an excess of elemental Se for 2 h at 60 °C in C_6D_6. For spectroscopic data see Table 5.

Asymmetric C=N-Hydrogenation; General Procedure

A 10-mL stainless steel autoclave equipped with a glass inlet and a magnetic stirring bar was charged under an argon atmosphere with the imine **5** (0.5 mmol) and I_2 (0.025 mmol). A Schlenk flask equipped with magnetic stirring bar was charged with $[Ir(cod)Cl]_2$ (1.68 mg, 2.5 μmol), the desired ligand **L1** or **L2** (5.5 μmol), and toluene (2 mL). After 10 min under stirring, the resulting soln was

transferred to the autoclave. The autoclave was pressurized with H_2 (40 bar) and the mixture stirred at r.t. for 16 h. After carefully releasing the pressure, conversion, and enantiomeric excess were determined by GC (Chirasil-Dex-CB, 25 m, 100–160 °C, 5 °C/min, 1.0 bar H_2): t_R = 18.7 (*S*)-**6**, 18.9 min (*R*)-**6**.

Single Crystal X-ray Diffraction

Data collection for **L1** and **L2** was done with MoKα radiation (INCOATEC microsource, multilayer optics, λ = 0.71073 Å) on a Bruker D8 goniometer with SMART CCD area detector; The SADABS[17] program was used for absorption correction of **L2** and PLATON[18] was used for multi-scan absorption correction of **L1**. The structures were solved by direct methods (SHELXS-97)[19] and refined by full matrix least-squares procedures based on F^2 with all measured reflections (SHELXL-97).[19] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions and refined using a riding model. Supplementary crystallographic data for **L1** (CCDC 882099) and **L2** (CCDC 882100) can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

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