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A Flexible Approach to Different Families of Bidentate P,P Ligands as Highly Efficient Ligands for Asymmetric Catalysis

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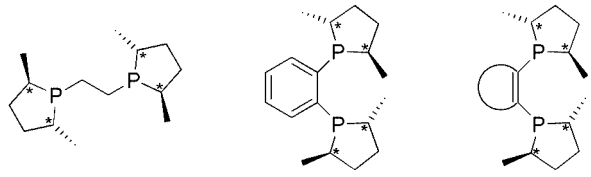
A novel and versatile approach has led to the synthesis of various classes of mono- and bidentate phospholane and phosphinite ligands based on a benzothiophene scaffold. The ligand functions in the bidentate ligands can be introduced independently and consecutively. A bis-phospolane ligand as well as its rhodium complex have been characterized by crystal-structure determinations. The bis-phospholane ligands were tested in the catalysed asymmetric homogeneous hydrogenation of dehydroamino acid derivatives, enamides and itaconates and gave *ee* values of up to 98.7 %.

Introduction

Chiral phosphanes play an important role as ligands in transition-metal-catalyzed asymmetric hydrogenation reactions and many very successful representatives such as DIOP,[1] DIPAMP[2] and BINAP[3] have been designed and synthesized over the past three decades.

More recently, with the BPE[4] (**1**) and especially the DuPHOS ligands[5] (**2**), a class of ligands that afford excellent selectivity in the Rh^{I}-catalyzed asymmetric hydrogenation of olefins has emerged.[6] The flexible design of these ligands with respect to variations of the backbone and/or of the phospholane allows in many cases a representative to be quickly identified that provides excellent hydrogenation results for a given substrate. Up to now, compared with the BPE ligands, the DuPHOS ligands with their rigid backbone have appeared to be more useful, and by changing the phospholane part of the DuPHOS ligand, numerous analogues with the same backbone have been prepared by the groups of Börner,[7] Zhang,[8] Rajanbabu[9] and others.[10]

In all these ligands the relative electronic properties as well as the bite angle remain almost constant.[11] Changing the backbone requires extra synthetic effort as the required bis-primary phosphanes are not commercially available. Such a change will alter the electronic nature of one or both of the phosphorus atoms and only relatively few phospholane-phosphane ligands of this type have been described.[12] As the bite angle is also affected, which has a profound effect on the performance of a ligand,[13] such variations in DuPHOS offer new handles for fine-tuning and thus have the potential to broaden the scope of phospholane-derived ligands.



1 **2** **3**

Our objective in this work was to be flexible with respect to the bite angle of our ligands and also to prepare bidentate ligands in which the electronic nature of the phosphorus could be modified in order to allow ligands of type **3** to be accessed in the most flexible manner.

This led us to consider heterocycles such as benzothiophene, *N*-alkylindoles and benzofuran as useful novel ligand backbones. In our strategy, attaching the first phosphorus atom P1 is achieved through electrophilic bromination at the 3-position followed by the reaction of the corresponding organometallic reagent with a suitable phosphorus electrophile. In the next step, the second phosphorus atom P2 is introduced either directly of after further functionalisation of P1 by heteroatom-assisted metallation of the backbone in the 2-position and the reaction of this species with a second phosphorus electrophile.

This strategy requires slight modifications for each of the particular backbones. For benzofuran, the derived 3-Grignard reagent is prone to fragmentation,[14] whereas for benzothiophene metal migration from the 3- to the 2-position is known to occur readily.[15] Apart from this, with some further adaptations other donor atoms instead of phosphorus can also be attached to the backbone in either

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step and thus an enormous variety of ligands becomes accessible by our approach.

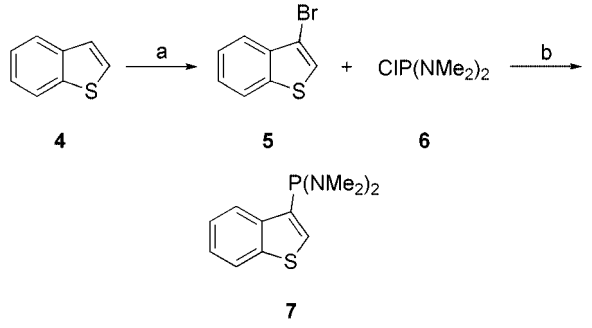
For geometrical reasons, the bite angle for all of these ligands can be expected to be larger than for ligands derived from 1,2-bis(phosphanyl)benzene such as DuPHOS and should increase from benzothiophene- through indole- to benzofuran-derived ligands. As for ligands with a large bite angle, irrespective of the electron density of the specific ligand, unusually high activities have been observed in asymmetric hydrogenation reactions with the derived Rh^I catalysts, for example, for Phanephos,[16] DiPFc[17] and the Ferrotane ligands.[18] This was considered to be a desirable feature of the new ligands.

Also, depending on the heteroatom in the backbone, the electron densities at the two phosphorus atoms will be affected. It is difficult to predict this effect, but ligands derived from the benzothiophene backbone can be expected to be more electron-rich than ligands derived from the 1,2-bis(phosphanyl)benzene backbone.[12e,12f]

In the following the synthesis of some mono- and bidentate P,P ligands derived from benzothiophene will be described. Also, the results of some initial hydrogenation reactions with cationic Rh^I catalysts derived from these ligands will be presented.

Results and Discussion

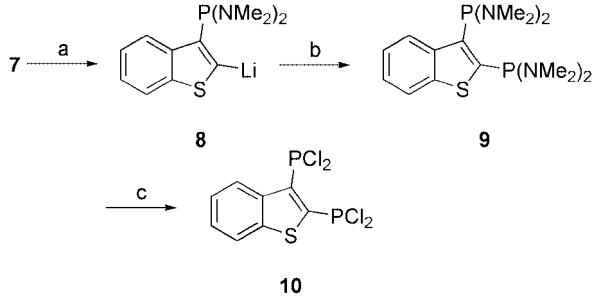
The bromination of benzothiophene **4** in the presence of sodium or potassium acetate has previously been reported,[19a,19b] but we found it more convenient to perform the bromination reaction in the absence of acetate.[19c] It was noticed that even when a slight excess (ca. 10%) of bromine was employed, conversion of benzothiophene was still incomplete. In the end, we chose to use an excess of 10% bromine as a compromise to obtain a good conversion of **4** into **5** (Scheme 1) without losing too much product due to over-bromination. The selectivity towards bromination at the 3-position is good and only a small quantity of 2-bromobenzothiophene was formed (ca. 3% by GC).



Scheme 1. Synthesis of **7**. Reagents and conditions: (a) 1.05 equiv. Br_2, 0–15 °C, 46%; (b) 1 equiv. **5** + 1.05 equiv. **6** added to 3 equiv. Mg in THF, 66%.

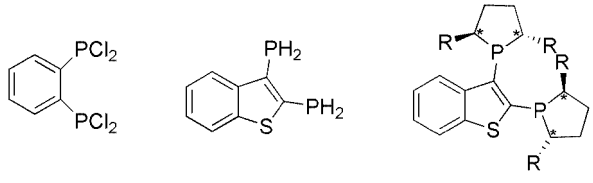
For the subsequent introduction of a phosphorus electrophile into the 3-position it is crucial that no migration of the metal from the 3- to the 2-position occurs in the intermediate species. In order to suppress this, we decided to trap the corresponding Grignard reagent immediately with the phosphorus electrophile. Thus, when an equimolar mixture of **5** and chlorobis(dimethylamino)phosphane[20] (**6**) in THF was added to excess magnesium turnings, the 3-substituted benzothiophene **7** was obtained in ca. 75–85% yield in a vigorous reaction. Very little product resulting from metal migration (<5% by GC) was formed under these conditions and thus **7** was not purified prior to the next step (Scheme 1).

The metallation of **7** with *n*BuLi in the presence of TMEDA is facile and the intermediate formed was quenched by the addition of a slight excess of **6** to give **9**. If desired, this intermediate can be isolated, but we found it more convenient to treat it directly with gaseous HCl to give **10** in a typical yield of ca. 75% based on **7** (Scheme 2).



Scheme 2. Synthesis of **10**. Reagents and conditions: (a) 1.1 equiv. *n*BuLi, 1.2 equiv. TMEDA, Et_2O, 2 h room temp.; (b) 1.1 equiv. **6**; (c) excess HCl_g, 75% overall.

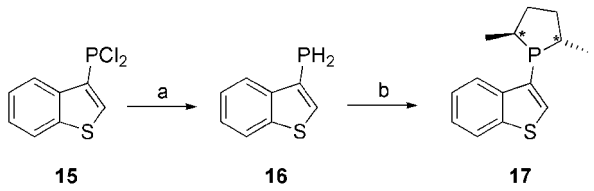
Compound **10** is a crystalline solid which can be handled in air for a short time without special precautions. It is an extremely versatile ligand precursor as it reacts with alcohols to give bis(phosphinite) ligands or with secondary amines to give, for example, diazaphospholidine ligands of the ESPHOS type.[21] Further, bidentate phosphanes are readily available from **10** by reaction with organometallic reagents. Interestingly, the only known analogue of **10** is **11**, which has a backbone related to that of DuPHOS. However, **11** is, by far, not as readily available as **10** as its synthesis either involves the use of mercury compounds[22a] or poses safety problems as *ortho*-lithiobromobenzene is formed as an intermediate.[22b]



The reduction of **10** with lithium aluminium hydride provides bis(phosphane) **12** in 60% yield. From **12** the DuPHOS analogues **13**, **14a** and **14b** were prepared essentially as described by Burk.[23] However, especially in large-scale preparations of DuPHOS and other ligands with pro-

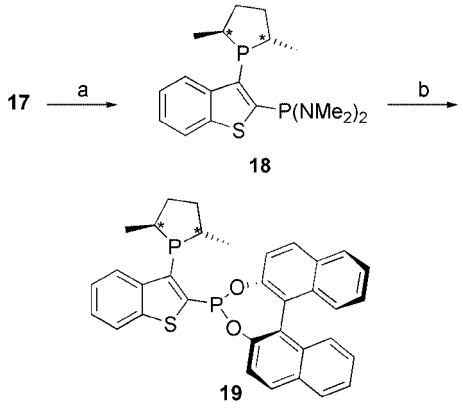
longed dwell times the reaction of *n*-butyllithium and also the deprotonated phosphane with THF becomes significant and causes considerable losses in yield as a result of the consumption of the base or the phosphane.[24] Thus, instead of *n*-butyllithium we selected lithium diethylamide (LDA) as the base because this was expected to result in a lower stationary concentration of the deprotonated phosphane and suppress phosphane consumption by "THF alkylation". As it turned out, at least on a small scale, the yields are similar to the reported yields[23] and in the course of the development of a process for the production of commercial quantities of these ligands a suitable approach was identified at Solvias AG.[25]

In order to demonstrate the synthetic flexibility of our strategy some other ligands were also prepared. From **7**, the corresponding dichlorophosphane **15** is readily available and reduction with lithium aluminium hydride provided **16** in 86% yield (Scheme 3).



Scheme 3. Synthesis of ligands **16** and **17**. Reagents and conditions: (a) $LiAlH_4$, THF, 87%; (b) (2*R*,5*R*)-hexanediol cyclic sulfate (1 equiv.), 2.2 equiv. KO*t*Bu, 64%.

This was converted into the crystalline monophospholane ligand **17**. Lithiation of **17** at the 2-position and reaction with **6** gave ligand **18**, which was treated with either the (*S*) or the (*R*) enantiomer of BINOL to give the corresponding phosphinite/phospholane ligands **19a** or **19b** (not drawn) essentially in quantitative yields (Scheme 4).



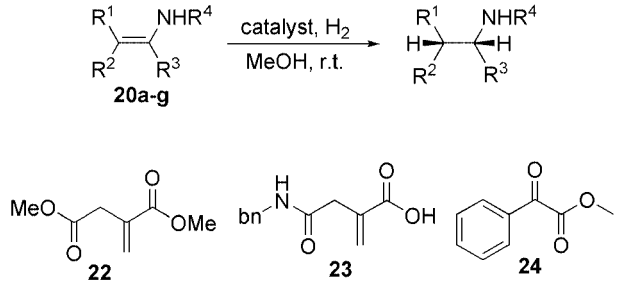
Scheme 4. Synthesis of ligands **18** and **19**. Reagents and conditions: (a) 2 equiv. TMEDA, 1.2 equiv. *n*BuLi, room temp., 2 h, then 1 equiv. **6**, 75%; (b) 1 equiv. (*S*)-BINOL, toluene reflux, 14 h, quant.

Ligands of type **19a** or **19b** are of interest for hydroformylation reactions and initial results for the hydroformylation of vinyl acetate and styrene look promising.[26]

Initial Hydrogenation Results

From ligands **13** and **14** the cationic Rh^I complexes $[(COD)Rh(ligand)]^+BF_4^-$ were prepared as precatalysts and then tested in the hydrogenation reactions of a selected set of hydrogenation substrates.

In the hydrogenation of the standard dehydroamino acid derivatives **20a** and **20b** a slight increase in the *ee* was observed at increased pressure and temperature for the first substrate, whereas the opposite trend was noticed for the second substrate (Scheme 5, Table 1). Enamides with a carbamate group at the nitrogen, such as **20c**, can be challenging because they do not coordinate well to the Rh^I catalyst.[5b] Thus we were pleased to notice that the hydrogenation of this substrate was complete within 6 hours under the given conditions providing the product in excellent optical purity.



Scheme 5. Substrates for hydrogenation reactions.

Some interesting trends were observed in the hydrogenation of enamide **20d**. Use of $[Rh(MeDuPhOS)(COD)]BF_4$ gave the product with a much higher *ee* than the catalyst derived from ligand **13**. Interestingly, the opposite trend was observed when the catalyst derived from EtDuPHOS was compared with the catalyst derived from **14**. Importantly, the *ee*s achieved are well in line with results obtained with other ligand–metal systems with these types of substrates.[27]

The utility of the Rh^I-derived catalysts was next tested in the hydrogenation of enamides leading to β-amino acid derivatives. With the (*E*)-enamides **20e** and **20f** the hydrogenation products were obtained in good-to-excellent *ee* and are in line with values reported by other groups.[28] The fact that the (*Z*)-enamide **20g** was also hydrogenated with high *ee* is important as usually the products from these enamides have a much lower *ee* and can be difficult to separate from the mixture of diastereoisomers of enamides usually obtained.

Hydrogenation of dimethyl itaconate (**22**) with the precatalyst derived from ligand **13** gave the (*S*) product in 94.8% *ee* and also the "inverse itaconate"[18a] **23** was hydrogenated rapidly with the same catalyst to give the product in 98.7% *ee* (Scheme 5, Table 1). Hydrogenation of **24** with this precatalyst was sluggish even at 40 bar at S/C = 100 and the product had an *ee* of only 34%. This relatively limited set of hydrogenation results and also recent results obtained with another substrate class clearly show the potential of these novel ligands.[29]

Table 1. Hydrogenation of enamide derivatives with [(COD)Rh(ligand)]BF_4 precatalysts in methanol. All reactions proceeded with complete conversion of the substrate.

Substrate	R1, R2, R3	R4	Cat. [mol-%]	$p(H_2)$ [bar]	Temp. [°C]	Ligand	*ee* [%]
20a	Ph, H, COOMe	Ac	0.5	1	25	**13**	94.4 *R*
20a	Ph, H, COOMe	Ac	0.5	5	35	**13**	94.9 *R*
20b	H, H, COOH	Ac	0.5	1	25	**13**	98.7 *R*
20b	H, H, COOH	Ac	0.5	5	35	**13**	98.2 *R*
20c	*p*-NO_2Ph, H, COOMe	CBz	0.1	10	35	**14**	98.7 *R*
20d	H, H, *m*-BnOPh	Ac	1.0	5	35	**13**	87.6
20d	H, H, *m*-BnOPh	Ac	1.0	5	35	**21a**[a]	93.0
20d	H, H, *m*-BnOPh	Ac	1.0	5	35	**14**	90.0
20d	H, H, *m*-BnOPh	Ac	1.0	5	35	**21b**[a]	86.8
20e	H, COOMe, Et	Ac	1.0	5	25	**13**	98.0
20f	H, COOMe, *i*-Bu	Ac	0.5	14	25	**14**	87.0
20g	COOMe, H, Me	Ac	1.0	5	25	**13**	90.0

[a] **21a**: MeDuPHOS; **21b**: EtDuPHOS.

NMR Discussion

The lack of C_2 symmetry in these ligands results in relatively complex NMR spectra, but this allows the assignment of all signals in the spectra in a relatively straightforward manner. For example, the assignment of the signals in the spectra of ligand **13** starts with the observation of an NOE signal between one aromatic proton and several aliphatic protons. Clearly, the aromatic proton must be 7-H, whereas the aliphatic protons must belong to the phospholane group attached to the C-3 atom. Following from this, a series of 1D TOCSY experiments allowed the set of protons belonging to either phospholane moiety to be identified. It is well established that the coupling of the methyl groups *syn* to the lone electron pair of the phosphorus is large (ca. 30 Hz) and small (ca. 0–5 Hz) for the methyl group *anti* to the lone pair.[30] Together with the C,H correlation obtained from an HSQC experiment this allowed the identification of the corresponding methyl groups in either phospholane moiety. The assignment of the other signals of the phospholanes as well as of the aromatic part of the ligand was derived from the COSY spectrum and the assignment of the phosphorus signals of either phospholane moiety was based on the observation of crosspeaks in a $^1H/^{31}P$ HETCOR experiment between the phosphorus atoms and the proton signals of the methyl groups and also of the CH protons that are *syn* to the lone pair of the phosphorus. The signals of the quaternary carbon atoms are very weak when directly observed but can be easily derived from the HMBC spectra. The assignments made for **13** are depicted in Figure 1.

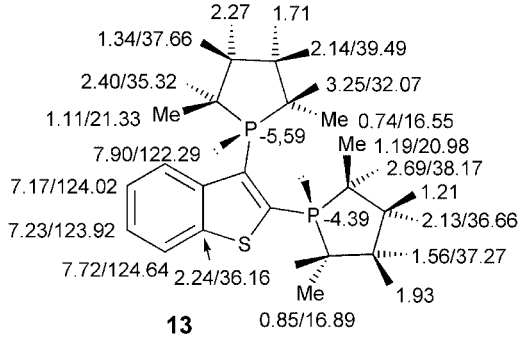


Figure 1. ^1H and ^{13}C NMR chemical shifts (ppm) for ligand **13**.

X-ray Structures

Ligand **14** is a crystalline solid and crystals suitable for X-ray structural analysis were obtained from an ethanolic solution. Interestingly, the angles of the P–C bonds relative to the thiophene ring are quite irregular (Figure 2) and deviate strongly from the (theoretical) value calculated for a regular pentagon (which would be 126°). This is also true for the rhodium complex [(**14**)Rh(COD)]BF_4 (Figure 3), which was also crystallized from an ethanolic solution. The coordination of the phosphorus atoms to rhodium leads to some compression of the P1–C1–C2 and P2–C2–C1 angles relative to the free ligand (121.7° vs. 126.2° and 114.6° vs. 116.5°, respectively). Contrary to our expectations, the bite angle P–Rh–P (85.2°) is almost identical to the bite angle in [Rh(MeDuPHOS)(COD)]SbF_6.[5b] A comparison of the bite angles of all known X-ray structures of DuPHOS-type

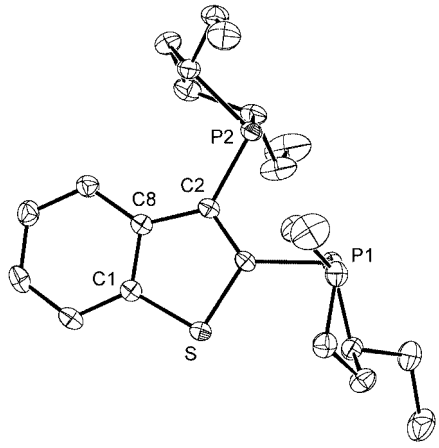


Figure 2. Displacement ellipsoid plot (PLATON)[31] of **14**. Ellipsoids are at the 30% probability level; all hydrogen atoms and the BF_4^- anion have been omitted for clarity. Selected bond angles: P2–C2–C8: 131.6°; P2–C2–C1: 116.5°; C2–C1–P1: 126.2°; P1–C1–S: 121.2°.

rhodium complexes has been carried out and shows a mean value for the P–Rh–P angle of 84.7°.[11a] For the MalPHOS ligand, based on a maleinic anhydride scaffold, a value of 86.1° has been calculated by DFT methods,[12d] while the same angle for UlluPHOS, based on a 3,4-substituted thiophene, is 85.86°.[12f] These values suggest that the bite angle at rhodium is quite insensitive to the nature of the ligand backbone. No correlation is seen between the bite angle and the enantioselectivities obtained in asymmetric hydrogenation reactions[9a] and no attempt has yet been made to the best of our knowledge to correlate catalytic activities with crystallographic parameters. The X-ray determination of another rhodium complex of the methyl derivative **13** has been reported.[11b]

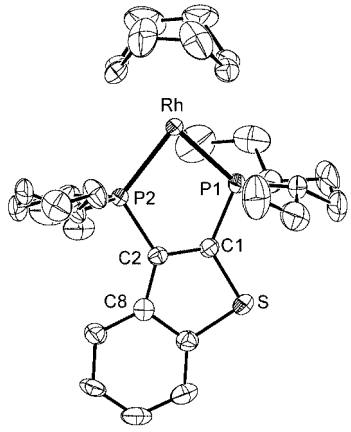


Figure 3. Displacement ellipsoid plot (PLATON)[31] of [(**14**)-Rh(COD)]BF_4. Ellipsoids are at the 30% probability level; all hydrogen atoms have been omitted for clarity. Selected bond angles: P2–C2–C8: 132.8°; P2–C2–C1: 114.5°; C2–C1–P1: 121.7°; P1–C1–S: 125.3°.

Summary and Conclusions

A new and very flexible strategy for the synthesis of various families of mono- and bidentate ligands has been presented. Initial results on selected applications of catalysts derived from these ligands show promising results and some ligands of this class are already commercially available from Solvias AG under the name of ButiPhane®.

Experimental Section

All reactions were carried out under nitrogen using Schlenk techniques. Solvents were dried and deoxygenated by standard procedures. NMR spectra were recorded with a Varian Mercury 300 (^{1}H: 300 MHz; ^{13}C: 75 MHz; ^{31}P: 121 MHz) and a Varian Unity 500 (^{1}H: 500 MHz; ^{13}C: 125 MHz; ^{31}P: 202 MHz) at ambient temperature. IR spectra were recorded with a Perkin–Elmer FT-IR model 1720 X spectrometer. Mass spectra were obtained with a Finnigan MAT 95 spectrometer using CI (isobutane as reactand gas) and SIMS recording techniques.

3-Bromobenzo[*b*]thiophene (5): A 2-L flask was charged with a solution of benzo[*b*]thiophene (187 g, 1.4 mol) in chloroform (500 mL) under argon. The mixture was cooled in an ice bath and bromine (246 g, 3.1 mol) in chloroform (200 mL) was added dropwise. The solvent was concentrated and the residue extracted with water and a 0.1 N sodium hydroxide solution. Evaporation of the solvent in vacuo gave the crude product. The product was further purified by vacuum distillation. Yield: 136.6 g (46%). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 7.40–7.50 (m, 1 H), 7.50–7.60 (m, 2 H), 7.70–7.80 (m, 2 H) ppm. ^{13}C NMR (CD_2Cl_2, 125 MHz): δ = 107.81 (1 C), 123.03, 124.02, 125.34, 125.60, 126.16 (5 C), 137.74, 138.87 (2 C) ppm.

Chlorobis(dimethylamino)phosphane (6): A 250-mL Schlenk flask was charged under argon with phosphorus trichloride (60 g, 0.44 mol). The flask was cooled to 0 °C and tris(dimethylamino) phosphane (142.9 g, 0.88 mol) was added under permanent cooling. The product was collected without purification as a light yellow liquid. Yield: 203 g (100%). ^{31}P NMR ($CDCl_3$, 121 MHz): δ = 164.15 ppm.

3-[Bis(dimethylamino)phosphanyl]benzo[*b*]thiophene (7): A 2-L flask fitted with a mechanical stirrer was charged with magnesium turnings (41.0 g, 1.69 mol) and THF (200 mL). Under an inert atmosphere a solution of 3-bromobenzo[*b*]thiophene (173 g, 0.81 mol) and chlorobis(dimethylamino)phosphane (145 g, 0.94 mol) in THF (300 mL) was added dropwise to the magnesium turnings over a period of 2½ h. The reaction mixture started to reflux and after the addition of the reagents had been completed, the mixture was maintained at reflux for another 1½ h. Then the mixture was cooled to ambient temperature and decanted from the magnesium turnings into a 2-L flask. After removal of the solvent on a rotavapor, the residue was extracted with hexane three times. The combined hexane extracts were concentrated to give a brown oil. The residue was extracted a further three times with ethyl acetate. Removal of the ethyl acetate from the combined extracts left an oil which by ^{1}H NMR was almost identical to the product *from* the hexane extractions. Distillation of the combined oils over a Vigreux column in vacuo gave the product as a pale yellow oil; b.p. 120 °C/0.018 mbar, yield = 136.5 g (66.7% based on 3-bromobenzo[*b*]thiophene). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.88 (d, $^3J_{H,P}$ = 9.4 Hz, 12 H, NCH_3), 7.37–7.46 (m, 2 H, 5-H, 6-H), 7.50 (d, J = 1.2 Hz, 1 H, 2-H), 7.94 (d, J = 6.7 Hz, 1 H, 7-H/8-H), 7.99 (d, J = 7.6 Hz, 1 H, 7-H/8-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 41.99 [d, $^2J_{C,P}$ = 15.8 Hz, 4 C, NCH_3], 122.45, 124.17 (d, J = 8.2 Hz), 124.24, 124.43, 129.96 (d, J = 9.8 Hz) (5 C, CH-Ar), 136.00 (d, J = 2.9 Hz), 140.26 (d, J = 18.9 Hz), 142.13 (d, J = 5.2 Hz) (3 C, C-Ar) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ = 93.80 ppm.

2,3-Bis[bis(dimethylamino)phosphanyl]benzo[*b*]thiophene (9): A 1-L flask was charged under argon with 3-[bis(dimethylamino)phosphanyl]benzo[*b*]thiophene (17.5 g, 69 mmol), TMEDA (10.5 g, 90 mmol) and 500 mL toluene. The mixture was cooled to 0 °C and then *n*BuLi (26.6 mL, 2.7 N, 69 mmol) was added dropwise over a period of 45 min while the temperature was held at around 5 °C. The reaction mixture was warmed to room temperature and stirred for 1 h. It was then cooled again to 5 °C and chlorobis(dimethylamino)phosphane (10.7 g, 69 mmol) was added over a period of 1 h. The flask was slowly warmed to room temperature and stirred for another 2 h. The product can be purified by evaporation of the solvent and vacuum distillation, but purification normally is not necessary. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.80 (d, $^3J_{H,P}$ = 9.0 Hz, 24 H, NCH_3), 7.22–7.37 (m, 2 H, 5-H, 6-H), 7.87 (d, J = 7.6 Hz, 1 H, 7-H/8-H), 8.23 (d, J = 8.2 Hz, 2 H, 7-H/8-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 41.92 (d, $^3J_{H,P}$ = 19.0 Hz), 41.95 (d, $^3J_{H,P}$ = 19.0 Hz), 42.66 (d, $^3J_{H,P}$ = 17.0 Hz), 42.71 (d, $^3J_{H,P}$ = 16.7 Hz) (4 C, NCH_3), 121.98, 123.63, 123.87, 125.06 (4 C, CH-

Ar), 136.73 (dd, J = 11.2, 15.6 Hz, 1 C, C-2), 143.30 (dd, J = 1.5, 3.3 Hz, 1 C, C-4/C-9), 143.62 (d, J = 8.4 Hz, 1 C, C-4/C-9), 152.92 (dd, J = 22.3, 33.2 Hz, 1C, C-3) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ = 97.37, 99.52 (AB, J = 28 Hz) ppm.

2,3-Bis(dichlorophosphanyl)benzo[*b*]thiophene (10): HCl gas was passed through the reaction mixture from the preparation of 2,3-bis[bis(dimethylamino)phosphanyl]benzo[*b*]thiophene. The reaction was monitored by ^{31}P NMR spectroscopy. After the starting material was no longer visible, the addition of HCl was continued for another 15 min. The precipitate was filtered off and washed with diethyl ether. The solvent from the combined organic phases was evaporated and the product collected as an orange-yellow solid. Yield: 14.6 g (63%). Purification by extraction of the solid with pentane in a Soxhlet extractor gave pale yellow crystals; m.p. 96 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.51–7.60 (m, 2 H, 5-H, 6-H), 7.93–7.97 (m, 1 H, 4-H/7-H), 8.62–8.68 (m, 1 H, 7-H/4-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 123.38 (1 C, C-7), 126.04 (1 C, C-6), 126.74 (1 C, C-4), 128.04 (1 C, C-5), 138.52, 144.22 (2 C, C-8, C-9), 142.77 (dd, J = 11, 50 Hz), 156.66 (dd, J = 24.9, 25 Hz) (2 C, C-2, C-3) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ = 133.99, 138.01 (AB, J = 450 Hz) ppm.

2,3-Bis(phosphanyl)benzo[*b*]thiophene (12): A 1-L three-necked flask was charged under argon with $LiAlH_4$ (2.7 g, 72.0 mmol) and THF (100 mL). Under reflux, 2,3-bis(dichlorophosphanyl)benzo[*b*]thiophene (8.0 g, 24 mmol) in diethyl ether (100 mL) was added. After the addition was complete, the reaction mixture was heated for another 1 h. The reaction mixture was cooled to room temperature and hydrolysed by careful addition of water. The solution was separated and the residue was extracted three times with pentane. The solvent was evaporated from the combined organic layers and the product purified by vacuum distillation. Yield: 3.0 g (63%); b.p. 91 °C/0.09 mbar. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.77 (dm, $J_{P,H}$ = 205 Hz, 2 H, PH_2), 4.02 (dm, $J_{P,H}$ = 207 Hz, 2 H, PH_2), 7.26–7.40 (m, 2 H, 5-H, 6-H), 7.68 (d, 1 H, J = 7.3 Hz, 7-H), 7.76 (d, 1 H, J = 7.8 Hz, 4-H) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ = –167.1, –150.8 (AB, $J_{P,P}$ = 65 Hz) ppm.

2,3-Bis[(2*R*,5*R*)-2,5-(dimethylphospholan-1-yl)]benzo[*b*]thiophene (13): A solution of the cyclic sulfate derived from (2*S*,5*S*)-hexane-2,5-diol (3.96 g, 22 mmol) in THF (250 mL) was degassed by bubbling argon through the solution at 0 °C for 1 h. 2,3-Bis(phosphanyl)benzo[*b*]thiophene (1.98 g, 10 mmol) was added to the degassed solution and under continuous cooling and vigorous stirring a solution of LDA [45 mmol, 22.3 mL of a 2 N solution in methyl *tert*-butyl ether (MTBE)] was added slowly. When the addition was complete, the mixture was warmed to ambient temperature. The solvent was removed on the rotavapor and water (ca. 100 mL) was added to the residue. The product was extracted with MTBE (100 mL) and obtained as a pale yellow oil by removal of the solvent from the dried (Na_2SO_4) extract. Yield: 1.91 g (53%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.74 (dd, J = 7.0, 10.2 Hz, 3 H, CH_3), 0.85 (dd, J = 7.0, 10.4 Hz, 3 H, CH_3), 1.11 (dd, J = 7.2, 19.1 Hz, 3 H, CH_3), 1.19 (dd, J = 6.9, 19.4 Hz, 3 H, CH_3), 1.21, 1.34, 1.56, 1.71, 1.93, 2.13, 2.14, 2.27 (m, 4 CH_2), 2.24, 2.40, 2.69, 3.25 (m, 4 C*H*), 7.17, 7.23 (2 "t", Ar-C*H*), 7.72, 7.90 (2 "d", Ar-C*H*) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 16.55 (s, CH_3), 16.89 (d, CH_3), 20.89, 21.33 (2 m, 2 CH_3), 32.07 (m, CH), 35.32 (m, CH), 36.16 (m, CH), 36.66 (s, CH_2), 37.27 (d, CH_2), 37.66 (t, CH_2), 38.17 (m, CH), 39.49 (d, CH_2), 122.29 (s, Ar-CH), 123.92 (s, Ar-CH), 124.02 (s, Ar-CH), 124.29 (s, Ar-CH), 124.64 (t, Ar-CH), 139.44, 142.85, 151.96 (Ar-C) ppm. ^{31}P NMR-($CDCl_3$, 202 MHz): δ = –5.59 (d, $J_{P,P}$ = 158.5 Hz), –4.39 (d, $J_{P,P}$ = 158.9 Hz) ppm.

2,3-Bis[(2*S*,5*S*)-2,5-(diethylphospholan-1-yl)]benzo[*b*]thiophene (14): A solution of the cyclic sulfate derived from (2*R*,5*RS*)-octane-2,5-diol (4.4 g, 21 mmol) in THF (250 mL) was degassed by bubbling argon through the solution at 0 °C for 1 h. 2,3-Bis(phosphanyl) benzothiophene (2.0 g, 10 mmol) was then added to the degassed solution and vigorously stirred before being added dropwise to a solution of LDA (50 mmol, 22.5 mL of a 2.2 N solution). When the addition was complete, the mixture was warmed to ambient temperature. The solvent was then removed on the rotavapor and water (ca. 100 mL) was added to the residue. The product was extracted with pentane (100 mL) and obtained as a white solid by removal of the solvent from the dried (Na_2SO_4) extract. Yield: 2.0 g (47%). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 0.82 (t, J = 7.3 Hz, 3 H, CH_3), 0.90 (t, J = 7.3 Hz, 3 H, CH_3), 0.92 (t, J = 7.3 Hz, 3 H, CH_3), 0.97 (t, J = 7.3 Hz, 3 H, CH_3), 1.28–1.37, 1.39–1.49, 1.54–1.67, 1.68–1.74, 1.77–1.87 (m, 10 H, CH_2), 2.00–2.22 (m, 3 H, CH, CH_2), 2.28–2.38 (m, 3 H, CH_2), 2.46–2.56 (m, 1 H, CH_2), 2.59–2.67, 3.17–3.24 (m, 2 H, CH) ppm. ^{13}C NMR (CD_2Cl_2, 125 MHz): δ = 14.05 (1 C, CH_3), 14.44 (2 C, CH_3), 14.72 (1 C, CH_3), 24.90, 25.22, 29.37, 27.78, 34.29, 34.43, 34.73, 37.12 (8 C, CH_2), 39.97, 43.62, 44.15, 47.55 (4 C, CH), 122.47, 124.15, 124.36, 125.32 (4 C, CH-Ar), 140.48, 143.09, 143.43, 153.07 (4 C, C-Ar) ppm. ^{31}P NMR (CD_2Cl_2, 202 MHz): δ = –12.10 (d, $J_{P,P}$ = 158. 2 Hz), –10.90 (d, $J_{P,P}$ = 155.7 Hz) ppm.

{2,3-Bis[(2*S*,5*S*)-2,5-diethylphospholan-1-yl]benzo[*b*]thiophene}(1,5-cyclooctadiene)rhodium(I) Tetrafluoroborate, [Rh(COD)(*S*)-EtButiPhane][BF_4]: A 50-mL Schlenk flask was charged with [Rh(COD)-acac] (0.861 g, 2.77 mmol) and THF (5 mL). A solution of the ligand (1.0 g, 2.77 mmol) and HBF_4·OEt_2 (0.450 g, 2.77 mmol), which had been diluted to 5 mL with THF, was added dropwise to the vigorously stirred solution at 65 °C. After about $^2/_3$ of the ligand/acid solution had been added, the catalyst started to precipitate. The crystallisation of the product went to completion when TBME (ca. 7 mL) was added very slowly to the reaction mixture. After cooling to ambient temperature, the catalyst was filtered off using a Schlenk filter and washed with a mixture of THF/MTBE (10 mL, 4:6, v/v). Drying in vacuo gave 1.018 g of orange crystals (55.6% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.87, 1.00, 1.01, 1.14 (4 t, J = 7.3 Hz, 3 H each, 4 CH_3), 1.27–1.43 (m, 2 H), 1.43–1.67 (m, 4 H), 1.78–2.17 (m, 7 H), 2.30–2.73 (m, 14 H), 2.99–3.17 (m, 1 H, CHP), 4.73–4.83, 5.02–5.13, 5.45–5.53, 5.66–5.76 (4 m, 1 H each, COD-CH), 7.46–7.58 (m, 2 H, 5-H, 6-H), 7.90, 7.96 (2 d, J = 8.1 Hz each, 1 H each, 4-H, 7-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.61 (dd, J = 2.6, 5.9 Hz), 14.69 (dd, J = 2.1, 5.1 Hz), 15.74 (dd, J = 3.1, 8.4 Hz), 16.25 (dd, J = 3.4, 8.7 Hz) (4 CH_3), 22.84 (s), 23.90 (s), 26.46 (d), 27.55 (d) (4 *C*H_2CH$_3$), 28.72 (s), 28.81 (s), 32.96 (s), 33.02 (s) (4 COD-*C*H_2), 33.46 (s), 34.54 (d), 34.69 (s), 34.88 (s) (4 phospholane *C*H_2), 44.29 (m), 45.18 (m), 46.77 (m), 53.50 (m) (4 AB*X* *C*HP), 91.24 (m), 93.99 (m), 104.13 (m), 108.45 (m) (4 AB*X* COD-*C*H), 124.85 (s), 124.87 (s) (C-4, C-7), 126.31 (s), 127.04 (s) (C-5, C-6), 135.66 (m), 143.21 (m), 150.47 (d), 152.90 (m) (C-2, C-3, C-8, C-9) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ = 56.16 (AB, $J_{P,P}$ = 23, $J_{P\text{-}1,Rh}$ = 145.7 Hz), 56.28 (AB, $J_{P\text{-}2,Rh}$ = 147.7 Hz) ppm.

2,3-Bis[(2*S*,5*S*)-2,5-diisopropylphospholan-1-yl]benzo[*b*]thiophene (14a): A solution of the cyclic sulfate derived from (3*R*,6*R*)-2,7-dimethyloctane-3,6-diol (12.2 g, 52 mmol) in THF (100 mL) was degassed by bubbling argon through the solution at 0 °C for 1 h. 2,3-Bis(phosphanyl)benzothiophene (4.9 g, 25 mmol) was then added to the degassed solution and to the vigorously stirred solution was then added dropwise a solution of LDA (120 mmol, 60 mL of a 2 N solution in THF). When the addition was complete, the mixture was warmed to ambient temperature. The solvent was

then removed and water (ca. 150 mL) was added to the residue. The product was extracted with MTBE (100 mL), the extracts dried with Na_2SO_4 and the solvent evaporated to yield 8.5 g (73%) of a pale yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.68–1.14 (m, 24 H), 1.18–2.43 (m, 14 H), 2.56 (m, 1 H), 3.17 (m, 1 H), 7.28 (m, 2 ArH), 7.80 (m, 1 ArH), 8.10 (d, J = 7.9 Hz, 1 ArH) ppm. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ = –16 (br.) ppm.

{2,3-Bis[(2*S*,5*S*)-2,5-diisopropylphospholan-1-yl]benzo[*b*]thiophene}-(1,5-cyclooctadiene)rhodium(I) Tetrafluoroborate, [Rh(COD)(*S*)-iPrButiPhane]BF$_4$: A 250-mL Schlenk flask was charged with [Rh(COD)]BF_4 (8.55 g, 21 mmol) and THF (45 mL). A solution of the ligand (10 g, 21 mmol) in THF (40 mL) was added dropwise to the vigorously stirred solution at 65 °C. After about $^2/_3$ of the ligand solution had been added, the catalyst started to precipitate. When MTBE (ca. 45 mL) was added very slowly to the reaction mixture, the crystallisation of the product went to completion. After cooling to ambient temperature the catalyst was filtered off and washed with a mixture of THF/MTBE (100 mL, 1:1 v/v). Drying in a vacuum gave 10 g of orange crystals (60% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.63 (d, J = 9.3 Hz, 3 H, CH_3), 0.80, 0.85, 0.87 (3 d, J = 9.3 Hz, 9 H, CH_3), 1.07, 1.15, 1.18 (3 d, J = 9.3 Hz, 9 H, CH_3), 1.26 (d, J = 9.3 Hz, 3 H, CH_3), 1.53–2.66 (m, 23 H), 3.05 (m, 1 H), 4.97, 5.06, 5.55, 5.70 (4 m, 4 H, COD), 7.55 (m, 2 H, ArH), 7.90 (m, 2 H, ArH), 8.00 (d, J = 10.1 Hz) ppm. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ = 50 (dd), 51 (dd) ppm.

3-(Dichlorophosphanyl)benzo[*b*]thiophene (15): A stream of gaseous HCl was passed through a solution of 3-[bis(dimethylamino)phosphanyl]benzo[*b*]thiophene (32.5 g, 129 mmol) in diethyl ether (250 mL) until no more HCl gas was absorbed and a sample showed complete conversion of the starting material by ^{31}P NMR spectroscopy. The colourless emulsion obtained was concentrated at normal pressure to give a light-brown crystalline residue. This was triturated three times with MTBE (ca. 50 mL each). Removal of the solvent from the combined extracts and distillation (107–112 °C at 0.1 mbar) gave the product (19.09 g, 63%) as a colourless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.48 (t, J = 7 Hz, 1 H, 6-H), 7.54 (t, J = 7.5 Hz, 1 H, 5-H), 7.94 (dm, J = 7.8 Hz, 1 H, 7-H), 8.14 (d, $J_{P,H}$ = 8.1 Hz, 1 H, 2-H), 8.46 (d, J = 8.1 Hz, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 123.39 (C-7), 124.43 (d, $^3J_{P,C}$ = 4.4 Hz, C-4), 125.36 (C-5), 125.92 (C-6), 134.82 (d, $^1J_{P,C}$ = 62.3 Hz, C-3), 137.10 (d, $^2J_{P,C}$ = 52.1 Hz, C-2), 137.33 (C-8), 141.77 (d, $^3J_{P,C}$ = 1.9 Hz, C-9) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ = 148.5 ppm.

3-Phosphanylbenzo[*b*]thiophene (16): Under nitrogen, a three-necked 1-L flask was charged with diethyl ether (200 mL) and a solution of $LiAlH_4$ in THF (58 mL of a 1 N solution, 58 mmol) was added. A solution of 3-(dichlorophosphanyl)benzo[*b*]thiophene (18.24 g, 77.6 mmol) in diethyl ether (ca. 40 mL) was added dropwise over about 30 min. An exothermic reaction took place and a solid formed. The excess $LiAlH_4$ was hydrolysed by the dropwise addition of NaOH (15 mL of a 4 N solution), which led to the formation of a colourless solid which precipitated readily. The supernatant liquid was removed using a cannula and the solid was extracted with further diethyl ether (20 mL). Evaporation of the solvent in vacuo gave the crude phosphane as a mobile oil which was further purified by vacuum distillation. Yield: 11.31 g (87%); b.p. 93 °C/0.036 mbar. ^{1}H NMR (C_6D_6, 300 MHz): δ = 3.59 (dd, $^1J_{P,H}$ = 200.5, ^4J = 1.2 Hz, 2 H, PH_2), 7.10 ("t", J = 7.4 Hz, 1 H, 6-H), 7.19 ("dt", $^2J_{H,P}$ = 7.5, ^4J = 1.2 Hz, 2-H), 7.20 (t, J = 7.4 Hz, 1 H, 5-H), 7.57 (d, J = 7.5 Hz, 1 H, 7-H), 7.70 (d, J = 7.5 Hz, 1 H, 4-H) ppm. ^{13}C NMR (C_6D_6, 75 MHz): δ = 122.06 (d, J = 16.1 Hz, C-2), 122.693 (C-7), 123.72 (C-4), 124.60, 124.63 (C-5, C-6), 134.54 (d, J = 35 Hz, C-2), 140.75 (d, J = 2.6 Hz, C-8), 142.22 (d, J = 2 Hz, C-9) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): δ = 163.1 ppm.

3-[(2*S*,5*S*)-2,5-Dimethylphospholan-1-yl]benzo[*b*]thiophene (17): A 1-L flask was charged with degassed THF (100 mL) and 3-phosphanylbenzo[*b*]thiophene (5.44 g, 32.7 mmol). A solution of KO*t*Bu (4.03 g, 36 mmol) in THF (20 mL) was added to this solution. The resulting red solution was transferred to a cooled (0 °C) degassed solution of the cyclic sulfate derived from (2*R*,5*R*)-hexane-2,5-diol (6.2 g, 34.4 mmol) in THF (40 mL). The resulting mixture was stirred for 2 h and the colour gradually turned pale yellow. More KO*t*Bu (4.03 g, 36 mmol) dissolved in THF (20 mL) was added and the mixture was stirred for another 2 h. Water (100 mL) and diethyl ether (100 mL) were then added and the organic layer was removed using a double-ended needle. The reaction mixture was extracted with a further diethyl ether (50 mL) and the organic layer was removed as described above. The combined organic layers were dried (sodium sulfate). Evaporation of the solvent gave a pale yellow oil, which was crystallized from ethanol (10 mL) at –20 °C. The crystals were removed by filtration through a Schlenk filter and dried to give 5.23 g (64.4%) of colourless crystals; m.p. 58 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.85 (dd, J = 6.7, 10.8 Hz, 3 H, CH_3), 1.40 (m, 1 H, 1 CH_2 at δ_C = 37.07), 1.41 (dd, J = 7.7, 19.9 Hz, 3 H, CH_3), 1.61 (dddd, J = 3.3, 6.0, 12.0, 18.3 Hz, 1 H, 1 CH_2 at δ_C = 37.35), 2.07 (ddm, J = 2, 5.9 Hz, 1 H, 1 CH_2 at δ_C = 37.35), 2.29 (m, 1 H, CH at δ_C = 35.09), 2.37 (m, 1 H, 1 CH_2 at δ_C = 37.07), 2.83 (m, 1 H, CH at δ_C = 36.18), 7.38 ("t", J = 7.0 Hz, 1 H, CH at δ_C = 124.66), 7.41 (d, J = 1.7 Hz, 1 H, 2-H), 7.44 ("t", J = 7 Hz, 1 H, CH at δ_C = 124.30), 7.92 ("d", J = 8.1, 1 H, CH at δ_C= 122.76), 8.22 ("d", 1 H, CH at δ_C = 124.04) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 15.83 (CH_3), 21.83 (d, J = 33.9 Hz, CH_3), 35.09 (d, J = 7.3 Hz, CH), 36.18 (d, J = 10.6 Hz, CH), 37.07 (CH_2), 37.35 (d, J = 4.0 Hz, CH_2), 122.76 (CH), 124.04 (CH), 124.23 (br. s, CH), 124.66 (br. s, CH), 129.17 (d, J = 6.7 Hz, C-2), 131.90 (d, J = 32.7 Hz, C-3), 140.89 (d, J = 4.6 Hz), 143.53 (d, J = 24.7 Hz) (C-8, C-9) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ = –8.59 ppm.

2-[Bis(dimethylamino)phosphanyl]-3-[(2*S*,5*S*)-dimethylphospholan-1-yl]benzo[*b*]thiophene (18): A 100-mL Schlenk flask was charged under argon with 3-[(2*S*,5*S*)-dimethylphospholan-1-yl]benzo[*b*]thiophene (4.2 g, 16.9 mmol) and TMEDA (2.0 g, 17 mmol). After the addition of anhydrous diethyl ether (30 mL), a solution of *n*BuLi (10.6 mL of a 1.6 N solution, 16.9 mmol) in hexanes was added. The mixture was stirred at ambient temperature overnight and then a solution of chlorobis(dimethylamino)phosphane (2.62 g, 17 mmol) in diethyl ether (10 mL) was added dropwise through a syringe. When the exothermic reaction had subsided the solvent was removed in vacuo and the residue was redissolved in pentane (30 mL). The LiCl was removed by filtration through a Schlenk filter and the solvent was removed again from the filtrate in vacuo. The residue was redissolved in pentane and the last traces of LiCl were filtered off as described above. Removal of the solvent from the filtrate in vacuo gave the product as yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.91 (dd, J = 7.3, 9.5 Hz, 3 H, CH_3 at δ_C = 16.61), 1.27 (dd, J = 6.9, 19.2 Hz, 3 H, CH_3 at δ_C = 21.55), 1.48, 2.37 (2 m, 1 H each, CH_2 at δ_C = 37.61), 1.92, 2.29 (2 m, 1 H each, CH_2 at δ_C = 39.37), 2.54 (m, 1 H, CH at δ_C = 35.19), 2.75 [d, J = 9.6 Hz, $N(CH_3)_2$, 12 H], 3.33 (m, 1 H, CH at δ_C = 32.62), 7.23–7.38 (m, 2 H, 5-H, 6-H), 7.85 (d, J = 7.4 Hz, 1 H, CH at δ_C = 122.63), 8.02 (d, J = 7.9 Hz, 1 H, CH at δ_C = 124.84) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 16.61 (d, J = 2.0 Hz, CH_3), 21.55 (d, J = 36.0 Hz, CH_3), 32.62 (dd, J = 6.5, 8.6 Hz, CH), 35.19 (dd, J = 1.6, 11.7 Hz, CH), 37.61 (d, J = 4.1 Hz, CH_2), 39.337 (br. s, CH_2), 41.65 (d, J = 17.9 Hz), 41.94 (dd, J = 2.2, 17.8 Hz) [$N(CH_3)_2$],

122.63 (CH), 123.68, 123.75 (C-5, C-6), 124.84 (CH), 134.03 (dd, J = 20.1, 41.3 Hz), 143.16 (s), 143.80 (d, J = 3.4 Hz), 159.31 (dd, J = 32.5, 37.5 Hz) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ = –3.51 (d, J = 119 Hz, P-3), 93.12 {d, P[N(CH_3)$_2$]$_2$} ppm.

(*S*,*S*)-4-{3-[(2*S*,5*S*)-Dimethylphospholan-1-yl]benzo[*b*]thiophen-2-yl}-3,5-dioxa-4-phosphacyclohepta[2,1-*a*:3,4-*a*′]dinaphthalene (19a): A 50-mL Schlenk flask was charged with a solution of 2-[bis(dimethylamino)phosphanyl]-3-[(2*S*,5*S*)-dimethylphospholan-1-yl]-benzo[*b*]thiophene (1.23 g, 33.5 mmol) in toluene (5 mL) under argon. (*S*,*S*)-Binaphthol (0.96 g, 33.5 mmol) was added to this solution and the mixture was heated at 110 °C overnight. The conversion was monitored by ^{31}P NMR spectroscopy and was completed within this time. The solvent was removed in vacuo and the residue was redissolved in CH_2Cl_2 (ca. 5 mL). The solvent was removed again and this was repeated once more in order to remove the last traces of toluene and dimethylamine. The product was formed as a colourless foam in quantitative yield. ^{1}H NMR/^{13}C HSQC: ($CDCl_3$, 500 MHz): δ = 1.05 (dd, J = 7.0, 10.0 Hz, 3 H, CH_3 at δ_C = 16.37), 1.47 (dd, J = 7.0, 19.5 Hz Hz, 3 H, CH_3 at δ_C = 20.97), 1.59 (m, 1 H, H at δ_C = 37.94), 2.04, 2.41 (2 m, 2×1 H, CH_2 at δ_C = 39.70), 2.41 (m, 1 H, H at δ_C = 37.94), 2.67 (m, 1 H, CHP at δ_C = 35.55), 3.43 (m, 1 H, CHP at δ_C = 34.11), 6.84 (d, J = 9 Hz, H at δ_C = 121.68), 7.31 (H at δ_C = 126.47), 7.34 (H at δ_C = 126.29), 7.36 (H at δ_C = 125.54), 7.40 (H at δ_C = 127.22), 7.43 (H at δ_C = 124.21), 7.45 (H at δ_C = 125.00), 7.48 (H at δ_C = 127.22), 7.49 (H at δ_C = 125.24), 7.65 (d, 2×J = 9.0 Hz, 2×1 H, H at δ_C = 121.68, H at δ_C = 129.99), 7.69 (d, J = 8.0 Hz, H at δ_C = 123.29), 7.86 (d, J = 8.5 Hz, H at δ_C = 128.59), 7.99 (d, J = 9.0 Hz, H at δ_C = 128.66), 8.06 (d, J = 9.0 Hz, H at δ_C = 130.85), 8.17 (d, J = 9.0 Hz, H at δ_C = 125.71) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz), additional quaternary C's: d 124.50, 125.00, 127.71, 131.31, 131.92, 132.89, 133.20, 141.35, 142.24, 144.13, 149.12, 150,28 ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ = –5.85 (d, $J_{P,P}$ = 195.5 Hz, P-3), 166.85 (P-2) ppm.

(*R*,*R*)-4-{3-[(2*S*,5*S*)-Dimethylphospholan-1-yl]benzo[*b*]thiophen-2-yl}-3,5-dioxa-4-phosphacyclohepta[2,1-*a*:3,4-*a*′]dinaphthalene (19b): This compound was prepared in exactly the same way as described for compound **19** using (*R*,*R*)-binaphthol. ^{31}P NMR ($CDCl_3$, 121 MHz): δ = –2.83 (d, $J_{P,P}$ = 194.3 Hz, P-3), 166.23 (P-2) ppm.

Hydrogenation Reactions: Substrates **20a**, **20b**, **22** and **24** were obtained from commercial sources and used as received. Substrates **20e**, **20f**,[28c] **20g**[32] and **23**[33] were prepared as previously reported. Substrate **20c** was obtained by the Wittig–Horner olefination[34a] of *p*-nitrobenzaldehyde with *N*-(benzyloxycarbonyl)trimethylphosphonoglycine[34b] in 75% yield. Substrate **20d** was obtained following a reported procedure[35a] from the ketone oxime and its spectral properties were as reported.[35b]

Typical Procedure: A 10-mL Schlenk flask with a magnetic stirring bar was charged with the respective catalyst. The Schlenk flask was evacuated and flushed with argon three times. Then the degassed solvent (3 mL) was added and the catalyst dissolved. Substrate **20** was transferred into a 25 mL Schlenk flask, which was purged by three cycles vacuum/argon flushing, and then dissolved in the solvent (3 mL). The catalyst and substrate solutions were transferred sequentially into a thermostatted stainless-steel autoclave (50 mL) equipped with a magnetic stirring bar under argon. The autoclave was submitted to a hydrogen pressure (10 bar) and the pressure released. After three cycles, the pressure and temperature were set to the described level and 20 min later magnetic stirring was started. After 17 h the autoclave was cooled to ambient temperature and the pressure released. The resulting solution was evaporated under reduced pressure (rotavapor, max. bath temp. 40 °C) to give the product mixture which was assayed for conversion by ^{1}H NMR spectroscopy and for *ee* by chiral HPLC.

Hydrogenation of 20a: Determination of conversion by ^{1}H NMR spectroscopy and *ee* by HPLC: Chiralcel OD (0.46×25 cm), hexane(95)/EtOH(5), flow 1.0 mL min, T = 25 °C, t (1st enantiomer) = 12.54 min, t (2nd enantiomer) = 14.12 min.

Hydrogenation of 20b: Determination of conversion by ^{1}H NMR spectroscopy and *ee* by HPLC: Chiralcel AD (0.46×25 cm), hexane(90)/EtOH(10), flow 1.0 mL min, T = 25 °C, t (1st enantiomer) = 7.49 min, t (2nd enantiomer) = 12.03 min.

Hydrogenation of 20c: Determination of conversion by ^{1}H NMR spectroscopy and *ee* by HPLC: Chiralcel OD (0.46×25 cm), hexane(90)/EtOH(10), flow 1.0 mL min, T = 25 °C, t (1st enantiomer) = 19.93 min, t (2nd enantiomer) = 23.58 min.

Hydrogenation of 20d: Determination of conversion by ^{1}H NMR spectroscopy and *ee* by HPLC: Chiralcel OJ (0.46×25 cm), hexane(80)/*i*PrOH(20), flow 0.8 mL min, T = 25 °C, t (1st enantiomer) = 13.4 min, t (2nd enantiomer) = 16.4 min.

Hydrogenation of 20e: Determination of conversion and *ee* by GC: LIPODEX E (0.25 mm×50 m), T = 145 °C isothermic, gas: H_2 (195 kPa), t (**20e**) = 3.6 min, t (1st enantiomer) = 6.9 min, t (2nd enantiomer) = 7.2 min.

Hydrogenation of 20f: Determination of conversion by ^{1}H NMR spectroscopy and *ee* by HPLC: Chiralcel OD (0.46×25 cm), hexane(98)/EtOH(2), flow 1.0 mL min, T = 25 °C, t (1st enantiomer) = 12.16 min, t (2nd enantiomer) = 13.45 min.

Hydrogenation of 20g: Determination of conversion by ^{1}H NMR spectroscopy and *ee* by HPLC: Chiralcel AD (0.46×25 cm), hex-

Table 2. Crystallographic data for compounds **14** and [(**14**)-Rh(COD)]BF_4.

Complex	**14**	[(**14**)Rh(COD)BF_4]
Empirical formula	$C_{24}H_{36}P_2S$	$C_{32}H_{48}BF_4P_2RhS$
Formula weight	418.53	716.46
Crystal size [mm]	0.8×0.4×0.4	0.60×0.15×0.15
Crystal habit	fragment of rod	trigonal prism
Crystal system	orthorhombic	trigonal
Space group	$P2_12_12_1$	$P3_2$
a [Å]	9.1657(16)	10.3398(12)
b [Å]	11.778(2)	
c [Å]	21.711(4)	26.290(3)
V [Å^3]	2343.8(7)	2434.1(5)
D [g cm^{-1}]	1.186	1.47
Z	4	3
Diffractometer	Bruker APEX CCD	NONIUS CAD4
T [K]	183	223
Wavelength [Å]	0.71073	0.71073
μ(Mo-K_α) [mm^{-1}]	0.282	0.734
θ range [°]	2.4–28.3	2.3–26.0
Index range (h, k, l)	–12/12, –15/15, –28/27	–11/12, –12/2, –32/32
Refl. collected	28259	12526
R_{int}	0.0319	0.1202
Unique refl. in refin.	5822	6356
Refl. with $I > 2\sigma(I)$	5595	5388
Param. refined	248	374
$R1$ [refl. with $I > 2\sigma(I)$]	0.0290	0.0393
$R1$ (all data)	0.0305	0.0759
$wR2$ (all data)	0.0728	0.0952
Flack param.	–0.04(5)	–0.01(3)
Goodness of fit	1.072	1.045
Diff. peak/hole [e Å^{-3}]	–0.19/0.32	–1.43/1.35

ane(90)/EtOH(10)/CF_3COOH(0.001), flow 1.0 mL min, T = 25 °C, t (1st enantiomer) = 13.47 min, t (2nd enantiomer) = 16.65 min.

Hydrogenation of 22: Determination of conversion and *ee* by GC: LIPODEX E (0.25 mm × 50 m), T = 90 °C, gas: He (140 kPa), t [(*S*) enantiomer] = 14.8 min, t [(*R*) enantiomer] = 15.5 min, t (**22**) 22.5 min

Hydrogenation of 24: Determination of conversion and *ee* by HPLC: Chiralcel OJ (0.46 × 25 cm), hexane(90)/*i*PrOH(10), flow 0.8 mL min, T = 25 °C, t (**24**) = 9.2 min, t [(*R*) enantiomer] = 12.0 min, t [(*S*) enantiomer] = 13.8 min.

X-ray Structure Determinations: Intensity data were collected with a Bruker D8 goniometer equipped with an APEX CCD detector for **14** and with an ENRAF-Nonius CAD4 diffractometer for [(**14**)Rh(COD)]BF_4 using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Crystal data, relevant parameters for data collection and convergence results are compiled in Table 2. The structures were solved by direct methods (SHELXS97[36]) and refined on F^2 (SHELXL97[37]) with anisotropic displacement parameters for all non-hydrogen atoms and with hydrogen atoms in a riding geometry. In view of the low linear absorption coefficients no absorption correction was performed for data from the serial detector and only a SADABS correction[38] was made for those collected on the area detector.

CCDC-226412 and CCDC-226413 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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