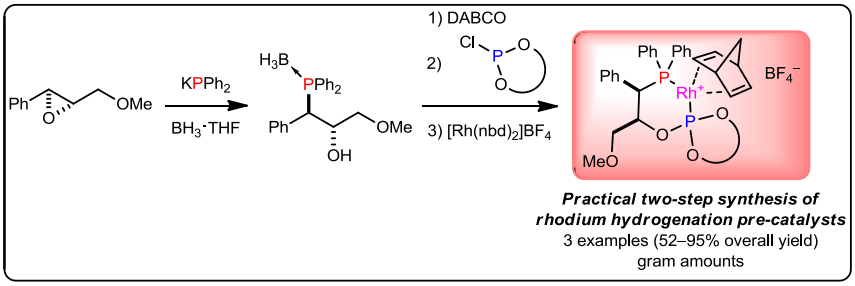
A Practical Synthesis of Rhodium Precatalysts for Enantioselective Hydrogenative Transformations

Bugga Balakrishna,[a,b] Anton Vidal-Ferran*[a,b]

[a] Institute of Chemical Research of Catalonia (ICIQ), Avgda. Països Catalans 16, 43007 Tarragona, Spain.
[b] Catalan Institution for Research and Advanced Studies (ICREA), Passeig Lluís Companys 23, 08010 Barcelona, Spain.
avidal@iciq.cat



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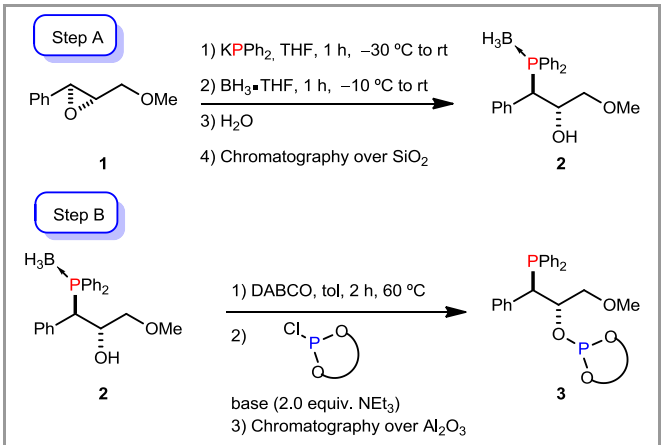
Abstract: Herein is described a practical method of preparing enantiopure rhodium(I) complexes that can be used as efficient catalysts for the asymmetric hydrogenation of functionalized alkenes, the hydrogenative kinetic resolution of vinyl sulfoxides and the desymmetrization of *meso*-dienes. All these rhodium precatalysts incorporate enantiopure phosphine-phosphite (P–OP) ligands as stereochemical directors of the hydrogenative transformations. The synthetic route starts with the ring-opening of an enantiopure Sharpless epoxy ether with a phosphorus nucleophile followed by isolation of the borane-protected phosphino alcohol derivative by crystallization. The subsequent cleavage of this borane complex, the *O*-phosphorylation of the resulting phosphino alcohol with the corresponding phosphorus electrophiles (chlorophosphite derivatives), and finally the complexation of the in situ generated P–OP ligands with $[Rh(nbd)_2]BF_4$, followed by crystallization, rendered the target precatalysts.

Key words: asymmetric hydrogenation; kinetic resolution; hydrogenative desymmetrization; phosphine-phosphite; rhodium catalysts; practical synthesis

The regulatory demands and environmental requests faced by the chemical and pharmaceutical industries have fueled the application of catalytic enantioselective methods to the preparation of biologically relevant compounds at industrial level. Asymmetric hydrogenation can be considered a well-established synthetic methodology that has already been incorporated into the standard "tool-box" of industrial chemists.[1] This transformation is considered a convenient method for the preparation of enantioenriched compounds, as catalytic amounts of a coordination compound (mainly Rh, Ru and Ir complexes) incorporating an enantiopure ligand (mostly phosphorus-containing derivatives[2]) mediate the addition of dihydrogen to prochiral C=C, C=N or C=O bonds with high yields and enantioselectivities.[3] Furthermore, hydrogenation reactions can easily be scaled up at industrial level as chemical companies have developed safe hydrogenation protocols.[1a] Despite the remarkably advanced state of the field, research efforts are still directed towards catalytic systems with higher activity and stereoselectivity. In other cases, researchers seek to improve the industrial profile of hydrogenation catalysts by developing easier preparation methods and by making sure they do not fall within the claims of any patent currently in force.

Our group has previously developed an array of structurally diverse P–OP ligands based on the use of enantiomerically pure Sharpless epoxy ether **1** as a starting material, which is transformed into the final ligands in two steps: ring-opening of the epoxide with a nucleophilic trivalent phosphorus derivative (step A, Scheme 1) followed by *O*-phosphorylation of the phosphino alcohol intermediate with trivalent phosphorus electrophiles (i.e. a chlorophosphite derived from an enantiomerically pure diol; step B, Scheme 1). As regards step A, the ring-opening proceeded smoothly at −30 °C to room temperature. The ring-opened product, which proved to be rather prone to oxidation, was protected in situ as the corresponding borane adduct **2** in order to make handling and storage easier. Borane complex **2** was isolated in high yield after column chromatography as a crystalline[4] and air-stable solid. In step B, the free phosphino alcohol was obtained by cleavage of the borane adduct **2**, using 1,4-diazabicyclo[2.2.2]octane (DABCO, 2.2 equiv.) at 60 °C in toluene for two hours.[5] After removing excess DABCO by a short chromatographic filtration through SiO_2 under inert atmosphere, the free phosphino alcohol was transformed into P–OP ligands by derivatization with the required chlorophosphite (1.1 equiv.) in the presence of a base (2.0 equiv. of NEt_3).[5] The final P–OP ligands were obtained in good yields after a careful chromatographic purification over neutral Al_2O_3 under inert atmosphere.[6]

We have also demonstrated the general ability of P–OP ligands to form suitable rhodium(I) precatalysts for hydrogenative reactions by reacting ligands **3** and $[Rh(nbd)_2]BF_4$ (nbd = norbornadiene).[6c,d,g,h] The $[Rh(nbd)(P–OP)]BF_4$ complexes were quantitatively formed in solution and could be isolated, if desired, by crystallization. For the sake of convenience, we have almost exclusively performed the asymmetric hydrogenations using $[Rh(nbd)(P–OP)]BF_4$ complexes, which had been generated in situ from $[Rh(nbd)_2]BF_4$ and a 10 mol% excess, with respect to rhodium, of the P–OP ligand **3**.



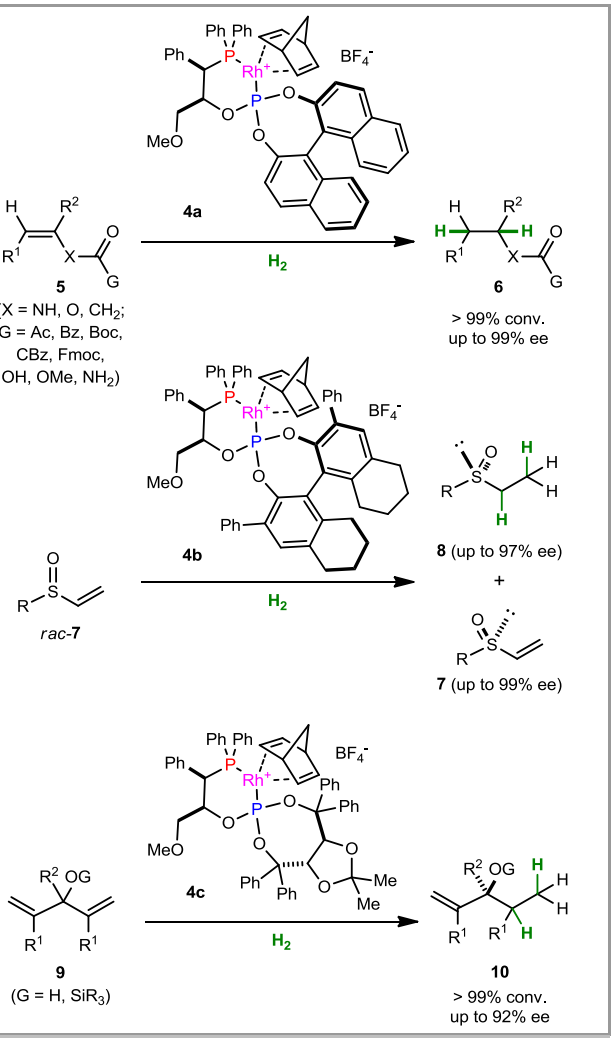
Scheme 1 Conventional synthetic strategy for the preparation of P–OP ligands

Interestingly, P–OP-based rhodium precatalysts **4a–c** efficiently mediate three different types of hydrogenative transformations providing high catalytic activities and enantioselectivities (up to 99% ee, Scheme 2). These transformations encompass the hydrogenation of functionalized alkenes[6] (see structure **5** in Scheme 2), the hydrogenative kinetic resolution of racemic vinyl sulfoxides[7] (substrates **7** in Scheme 2) and the hydrogenative desymmetrization of *meso*-dienes[8] (substrates **9** in Scheme 2). Taking these results into account, we considered that by developing a practical method for the preparation of complexes **4a–c** in gram amounts, the "asymmetric catalytic community" could gain easy access to our precatalysts for enantioselective hydrogenations and benefit by applying them to their own transformations of interest. Thus, we describe herein our efforts to develop and optimize a practical preparation method for rhodium precatalysts **4a–c**.

For the optimization of the ring-opening step (step A in Scheme 1), we took advantage of the crystallinity of compound **2** and developed crystallization conditions for isolating the target compound. Thus, ring-opening was basically performed under the same conditions as those previously used in the group (molar ratio of $KPPh_2$:**1**:BH_3 = 1:1.02:3).[4,6a] After an aqueous work-up of the reaction mixture, product **2** was extracted, dried and recrystallized from an EtOAc:hexane mixture (see experimental section for details). The solution containing product **2** was filtered while hot and the product was isolated as a crystalline material after leaving it standing at 5 °C for a few hours (86% yield). Both the yield and the spectroscopic data were in agreement with those previously reported[4,6a,6b] using the usual synthetic protocol[6a-g] that involves a chromatographic purification over SiO_2 (80% average yield for 6 experiments).

Next, we envisaged that the preparation of the target rhodium precatalysts **4a–c** could be accomplished in three consecutive synthetic steps starting from the borane-protected phosphino alcohol **2** (Scheme 3): first, borane cleavage; second, *O*-phosphorylation; and last, complexation with $[Rh(nbd)_2]BF_4$ as the metal precursor, where we planned to use this rhodium derivative as the limiting reagent of the synthetic sequence. We also decided to perform these three steps with no chromatographic separation as we expected to be able to isolate complexes **4a–c** by crystallization.

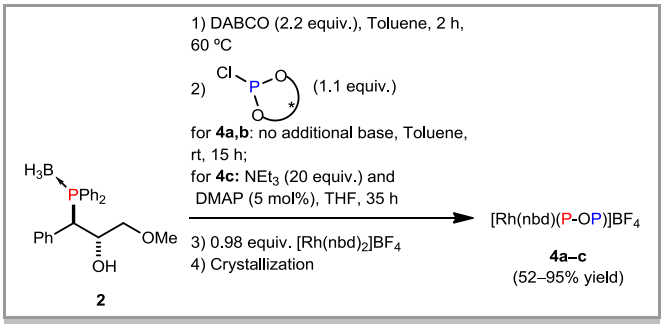
Regarding borane cleavage, the free phosphino alcohol was quantitatively obtained by deprotection of **2** using DABCO (2.0 equiv.) in toluene at 60 °C for 2 hours. The in situ generated phosphino alcohol was subsequently derivatized by treatment with the corresponding chlorophosphites (1.1 equiv.). In particular, for the chlorophosphites leading to rhodium complexes **4a** and **4b**, no additional base was required for achieving complete *O*-phosphorylation. DABCO, which was present in excess in the reaction media from the borane-cleavage step, sufficed for quantitatively mediating the reaction between the free phosphino alcohol and the chlorophosphite. However, the reaction of the free diphenylphosphino alcohol with the chlorophosphite leading to **4c** proceeded in THF at a slower rate and required the addition of a base (NEt_3, 20 equiv. with respect to the chlorophosphite) and catalytic amounts of *N,N*-dimethylpyridin-4-amine (DMAP, 5 mol%).[9] In all cases the *O*-phosphorylation reactions were monitored by $^{31}P\{^1H\}$ NMR spectroscopy in order to optimize the reaction times (see experimental procedures for details).



Scheme 2 Lead P–OP-based rhodium precatalysts for enantioselective hydrogenative transformations

The *O*-phosphorylation reaction mixtures toward complexes **4a** and **4b** were filtered through a short SiO_2 pad. The resulting material was allowed to react with $[Rh(nbd)_2]BF_4$ (ca. 0.98 equiv. with respect to the amount of P–OP ligand, which was roughly estimated by integration of the ^{31}P NMR spectra). The Rh–(P–OP) complexes **4a** and **4b** were isolated by crystallization in 77% and 95% overall yield respectively (referring to the amount of Rh–precursor). For the preparation of complex **4c**, a slightly modified procedure was followed. In this case the ligand was purified by crystallizing most of the P-containing impurities out of the solution after removing the solvents from the *O*-phosphorylation step. A complexation process analogous to that previously described was then followed (52% yield, see experimental procedures for details).

The $^{31}P\{^1H\}$ NMR spectra of **4a–c** showed two sharp doublets of doublets at around 29 ppm (phosphino group) and 135 ppm (phosphite groups) for each rhodium complex. The multiplicity of phosphorus signals is due to a direct $^{31}P–^{103}Rh$ coupling (average $^1J_{P\text{-}Rh} \approx 266$ Hz for phosphite and $^1J_{P\text{-}Rh} \approx 146$ Hz for phosphine groups) along with a geminal $^{31}P–^{31}P$ coupling (average $^2J_{P\text{-}P} \approx 68$ Hz). The rest of the NMR data and HRMS measurements unequivocally confirmed the structure of rhodium complexes **4a–c**.



Scheme 3 Preparation of Rh–(P–OP) complexes **4a–c**

In conclusion, we have developed and optimized a practical synthesis for "lead" enantiopure rhodium complexes derived from P–OP ligands. We have previously reported that these rhodium complexes have been efficiently applied as precatalysts in a number of enantioselective hydrogenative transformations. The herein described synthetic protocols may enable these efficient hydrogenation catalysts to be easily accessed by the "asymmetric catalytic community".

All manipulations and reactions were run under inert atmosphere using anhydrous solvents in either a glove box or with standard Schlenck-type techniques. All solvents were dried by using a Solvent Purification System (SPS). ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts are quoted in ppm relative to residual solvent peaks, whereas $^{31}P\{^1H\}$ NMR chemical shifts are quoted in ppm relative to 85% phosphoric acid in water. $^{11}B\{^1H\}$ NMR and $^{19}F\{^1H\}$ NMR chemical shifts are quoted in ppm relative to $BF_3{\cdot}OEt_2$ in $CDCl_3$. High resolution mass spectra (HRMS) were recorded by using the ESI ionization method in positive mode. Melting points were measured in open capillaries and are uncorrected.

Experimental Procedures:

Borane Complex 2. A solution of $KPPh_2$ in THF (15.7 mmol, 31.4 mL of a 0.5 M solution) was added dropwise under Ar to a cooled solution (–30 °C) of **1** (16.0 mmol, 2.623 g) in dry THF (50 mL). The mixture was stirred for 1h at this temperature and then slowly allowed to reach rt and stirred for one additional hour. The mixture was then cooled at –10 °C and BH_3•THF (47.0 mmol, 47 mL of a 1M solution) was added dropwise. The mixture was stirred for 1h at this temperature and then allowed to reach rt and stirred for one further hour. The reaction mixture was quenched with water (50 mL) and the two phases were separated. The aqueous phase was extracted with EtOAc (3×50 mL). The combined organic phases were washed with brine (2×50 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The resulting residue was re-dissolved in hexane:EtOAc (70:30, 75 mL, 10.9 mL per gram of crude mixture) while heating at 50 °C. The solution was filtered while hot and allowed to stand overnight at 5 °C. A white solid was formed, which was filtered, washed with hot hexane and dried in vacuo (3.826 g, 10.50 mmol, 66.9% yield). The mother liquors were concentrated in vacuo and the crystallization process was repeated in hexane:EtOAc (70:30, 25 mL, 12.4 mL per gram of crude mixture). A second fraction of compound **2** was obtained (1.106 g, 3.04 mmol, 19.3% yield). mp 108–110 °C (reported value:[6a] 117.1–117.6); $[\alpha]_D^{25}$ –147.3 (*c* 0.1, $CHCl_3$) (reported value:[6a] $[\alpha]_D^{25}$ –154.2 (*c* 1.0, $CHCl_3$). Spectroscopic data were in agreement with the reported ones.[6a]

Rh–(P–OP) complex 4a. The phosphino-borane adduct **2** (1.046 g, 2.87 mmol) was azeotropically dried with 16 mL of toluene. DABCO (0.724 g, 6.45 mmol) was added to the residue and after three freeze-and-thaw cycles under Ar, 18 mL of toluene were syringed into the Schlenk tube containing compound **2** and DABCO. The solution was stirred for 2 h at 60 °C. The residue was left to cool down to rt and a freshly prepared solution of the chlorophosphite[10] (1.108 g, 3.16 mmol, 36 mL of toluene) was added dropwise to the previous solution. The reaction mixture was left to stir for 15 h at rt. The reaction mixture was filtered through a short, dry, deoxygenated SiO_2 pad (5 mL) and the SiO_2 subsequently

washed with dry toluene (2 × 6.0 mL). The filtrate was collected in a Schlenk flask under inert atmosphere and concentrated in vacuo to obtain a spongy white solid that corresponded to the raw phosphine-phosphite ligand (1.554 g, ca. 2.10 mmol, ca. 90% purity by integration of the signals of the ligand with respect to the rest of the signals in the ^{31}P NMR spectrum). A freshly prepared solution of the raw phosphine-phosphite ligand (1.554 g, ca. 2.10 mmol, 16 mL of dichloromethane) was slowly added to a solution of $[Rh(nbd)_2]BF_4$ (0.762 g, 2.04 mmol, 12 mL of dichloromethane) and stirred at rt for 4 h. After this period of time, 75% of the solvent amount was evaporated off in vacuo. Anhydrous Et_2O (24 mL) was carefully layered onto the remaining solution of the complex. With gradual stirring of the solution, an orange solid was formed. The mother liquors were filtered off and the residue was washed with anhydrous Et_2O (2 x 10 mL) and dried in vacuo to afford 1.49 g (1.57 mmol, 77% overall yield with respect to $[Rh(nbd)_2]BF_4$) of complex **4a** as an orange powder. mp 207–209 °C; $[\alpha]_D^{25}$ +13.0 (*c* 0.1, THF). Spectroscopic data were in agreement with the reported ones.[6b]

Rh–(P–OP) complex 4b. The same protocol as for **4a** was used, with the following amounts of reagents (solvent amounts were adapted so that concentrations were the same): compound **2** (1.578 g, 4.33 mmol), DABCO (1.042 g, 9.29 mmol), chlorophosphite[11] (2.54 g, 4.97 mmol) and $[Rh(nbd)_2]BF_4$ (1.084 g, 2.90 mmol). A spongy white solid that corresponded to the raw phosphine-phosphite ligand (2.74 g, ca. 2.96 mmol, ca. 89% purity by integration of the signals of the ligand with respect to the rest of the signals in the ^{31}P NMR spectrum) was obtained. After following a crystallization process identical to that described above, 3.06 g (2.76 mmol, 95% overall yield with respect to $[Rh(nbd)_2]BF_4$) of complex **4b** as an orange powder were obtained.

mp 224.3–226.3 °C; $[\alpha]_D^{25}$ +52.7 (*c* 0.12, THF).

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.02–8.00 (m, 2H, H_{arom}), 7.85–7.82 (m, 2H, H_{arom}), 7.72–7.30 (m, 14H, H_{arom}), 7.19–7.03 (m, 5H, H_{arom}), 6.71–6.61 (m, 4H, H_{arom}), 5.95 (bs, 1H, =C*H* vinylic, nbd), 5.41 (bs, 1H, =C*H* vinylic, nbd), 4.77 (bs, 1H, =C*H* vinylic, nbd), 4.42 (bs, 1H, =C*H* vinylic, nbd), 4.18 (bs, 1H, C*H* allylic, nbd), 3.88 (bs, 1H, 1H, C*H* allylic, nbd), 3.83–3.70 (m, 2H, C*H*-PPh_2 and C*H*-OPO), 3.07–2.92 (m, 7H, OCH_3 and 2 x CH_2 *o*-Ph-H8-BINOL), 2.80–2.61 (m, 3H, C*H*H-OMe and 1 x CH_2 *o*-Ph-H8-BINOL), 2.49–2.36 (m, 3H, CH*H*-OMe and 1 x CH_2 *o*-Ph-H8-BINOL), 1.97–1.67 (m, 10H, CH_2 nbd and 4 x CH_2 *o*-Ph-H8-BINOL).

^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2) δ = 142.20 ($C_{q\ arom}$), 142.16 ($C_{q\ arom}$), 141.9 ($C_{q\ arom}$), 141.8 ($C_{q\ arom}$), 139.35 ($C_{q\ arom}$), 139.34 ($C_{q\ arom}$), 138.38 ($C_{q\ arom}$), 138.37 ($C_{q\ arom}$), 137.2 ($C_{q\ arom}$), 137.10 ($C_{q\ arom}$), 137.09 ($C_{q\ arom}$), 136.5 ($C_{q\ arom}$), 136.2 ($C_{q\ arom}$), 135.4 (CH_{arom}), 135.3 (CH_{arom}), 132.6 ($C_{q\ arom}$), 132.2 ($C_{q\ arom}$), 131.85 ($C_{q\ arom}$), 131.82 ($C_{q\ arom}$), 131.6 (CH_{arom}), 131.54 (CH_{arom}), 131.48 (CH_{arom}), 131.44 (CH_{arom}), 131.40 (CH_{arom}), 131.35 (CH_{arom}), 131.27 (CH_{arom}), 130.3 (CH_{arom}), 129.8 (CH_{arom}), 129.65 (CH_{arom}), 129.57 (CH_{arom}), 129.3 (CH_{arom}), 128.8 (CH_{arom}), 128.7 (CH_{arom}), 128.6 (CH_{arom}), 128.4 (CH_{arom}), 128.0 (CH_{arom}), 127.94 (CH_{arom}), 127.92 (CH_{arom}), 127.4 (CH_{arom}), 126.2 ($C_{q\ arom}$), 125.8 ($C_{q\ arom}$), 103.7 (=*C*H vinylic, nbd), 100.6 (d, *J* = 12.3 Hz, =*C*H vinylic, nbd), 93.1 (=*C*H vinylic, nbd), 79.8 (=*C*H vinylic, nbd), 75.4 (dd, *J* = 6.1 Hz, *C*H-OPO), 72.4 (CH_2 nbd), 69.8 (dd, *J* = 8.8 Hz, *C*H_2-OMe), 58.2 (OCH_3), 55.6 (*C*H allylic, nbd), 55.3 (*C*H allylic, nbd), 42.0 (d, *J* = 28.7 Hz, *C*H-PPh_2), 29.3 (CH_2), 29.2 (CH_2), 27.8 (CH_2), 27.7 (CH_2), 22.6 (CH_2), 22.53 (CH_2), 22.46 (CH_2), 22.4 (CH_2).

^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ = 130.3 (dd, *J* = 263.8, 69.7 Hz, *P*–O), 23.7 (dd, *J* = 146.0, 69.7 Hz, *P*–C).

^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2): δ = –1.1 (s, *B*F_4).

^{19}F{^{1}H} NMR (376 MHz, CD_2Cl_2): δ = –153.2 (s, B*F*$_4$).

HRMS-ESI: *m/z* $[M - BF_4]^+$ calcd for $C_{61}H_{58}O_4P_2Rh$: 1019.2860; found: 1019.2865.

Rh–(P–OP) complex 4c. The same experimental protocol as for **4a** was used, with the following amounts of reagents (solvent amounts were adapted so that concentrations were the same): compound **2** (2.475 g, 6.80 mmol), DABCO (1.675 g, 14.95 mmol), chlorophosphite[12] (3.98 g, 7.50 mmol) and $[Rh(nbd)_2]BF_4$ (0.690 g, 1.85 mmol). Additionally, the following changes to the original recipe were made. After the borane cleavage, the solvent was removed and substituted by THF (135 mL). NEt_3 (19 mL, 136 mmol) and DMAP (0.415 g, 0.34 mmol) were added to the reaction mixture under N_2. A spongy white solid that corresponded to the raw phosphine-phosphite ligand (2.715 g, ca. 1.83 mmol, ca. 58% purity by integration of the signals of the ligand with respect to the rest of the signals in the ^{31}P NMR spectrum) was obtained after precipitating (40 mL, hexane:Et_2O 75:25) and filtering out *P*-containing impurities (this precipitation/filtration process was repeated twice). The rhodium complex obtained as indicated for **4a** was recrystallized by layering hexane (15 mL) onto a solution of the complex in DCM (5 mL). Compound **4c** was isolated as an orange powder (1.07 g, 0.95 mmol, 52% overall yield with respect to $[Rh(nbd)_2]BF_4$) after filtering, washing with anhydrous Et_2O (2 x 10 mL) and drying in vacuo.

mp 182–185 °C; $[\alpha]_D^{27}$ +324.0 (*c* 0.10, THF).

^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.94–7.90 (m, 2H, H_{arom}), 7.82–7.78 (m, 1H, H_{arom}), 7.72–7.69 (m, 2H, H_{arom}), 7.59–7.40 (m, 14H, H_{arom}), 7.33–7.13 (m, 10H, H_{arom}), 7.05–6.99 (m, 4H, H_{arom}), 6.64–6.60 (m, 2H, H_{arom}), 6.16 (bs, 1H, =C*H* vinylic, nbd), 5.46 (d, *J* = 8.0 Hz, 1H, OC*H*-CHO, TADDOL), 5.33 (bs, 1H, =C*H* vinylic, nbd), 5.26 (bs, 1H, =C*H* vinylic, nbd), 5.14 (d, *J* = 8.0 Hz, 1H, OCH-C*H*O, TADDOL), 4.85 (bs, 1H, =C*H* vinylic, nbd), 4.33 (bs, 1H, C*H* allylic, nbd), 4.04 (bs, 1H, 1H, C*H* allylic, nbd), 3.94 (d, *J* = 8.0 Hz, 1H, C*H*-PPh_2), 3.36–3.31 (m, 1H, C*H*-OPO), 2.92 (s, 3H, OCH_3), 2.31 (dd, *J* = 9.4 Hz, 1H, C*H*H-OMe), 1.95–1.92 (m, 1H, C*H*H nbd), 1.79–1.74 (m, 2H, CH*H*-OMe and CH*H* nbd), 1.10 (s, 3H, CH_3, TADDOL), 0.34 (s, 3H, CH_3, TADDOL).

^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ = 144.3 ($C_{q\ arom}$), 144.2 ($C_{q\ arom}$), 143.8 ($C_{q\ arom}$), 139.72 ($C_{q\ arom}$), 139.66 ($C_{q\ arom}$), 138.6 ($C_{q\ arom}$), 134.9 (CH_{arom}), 134.8 (CH_{arom}), 132.8 (CH_{arom}), 132.43 (CH_{arom}), 132.35 (CH_{arom}), 131.6 ($C_{q\ arom}$), 130.91 (CH_{arom}), 130.89 (CH_{arom}), 130.4 ($C_{q\ arom}$), 130.1 (CH_{arom}), 130.0 (CH_{arom}), 129.0 (CH_{arom}), 128.93 (CH_{arom}), 128.90 (CH_{arom}), 128.7 (CH_{arom}), 128.64 (CH_{arom}), 128.61 (CH_{arom}), 128.5 ($C_{q\ arom}$), 128.3 (CH_{arom}), 128.2 ($C_{q\ arom}$), 127.9 (CH_{arom}), 127.7 (CH_{arom}), 127.2 (CH_{arom}), 126.9 (CH_{arom}), 114.0 (*C*-Me_2, TADDOL), 95.8 (=*C*H vinylic, nbd), 95.7 (=*C*H vinylic, nbd), 90.8 (d, *J* = 19.1 Hz, O*C*-Ph_2, TADDOL), 90.2 (d, *J* = 17.6 Hz, O*C*-Ph_2, TADDOL), 88.3 (=*C*H vinylic, nbd), 87.4 (=*C*H vinylic, nbd), 80.6 (d, *J* = 3.2 Hz, O*C*H-CHO, TADDOL), 78.5 (d, *J* = 4.6 Hz, OCH-*C*HO, TADDOL), 74.5 (d, *J* = 7.9 Hz, *C*H-OPO), 71.5 (CH_2 nbd), 68.7 (dd, *J* = 8.7 Hz, *C*H_2-OMe), 58.3 (OCH_3), 55.6 (*C*H allylic, nbd), 54.8 (*C*H allylic, nbd), 40.6 (d, *J* = 29.7 Hz, *C*H-PPh_2), 27.0 (CH_3, TADDOL), 25.5 (CH_3, TADDOL).

^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ = 108.0 (dd, *J* = 267.0, 68.1 Hz, *P*–O), 26.4 (dd, *J* = 148.1, 68.1 Hz, *P*–C).

^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2): δ = –1.1 (s, *B*F_4).

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HRMS-ESI: *m/z* $[M - BF_4]^+$ calcd for $C_{60}H_{58}O_6P_2Rh$: 1039.2758; found: 1039.2772.

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Supporting Information

Supporting information for this Article is available online at https://www.thieme-connect.de/DOI/DOI?10.1055/s-0035-1561360

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(2) See for example: (a) *Phosphorus Ligands in Asymmetric Catalysis*, 1st ed.; Börner, A., Ed.; Vols. I-III; Wiley-VCH: Weinheim, **2008**. (b)

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(3) See for example: (a) *Handbook of Homogeneous Hydrogenation*, 1st ed.; deVries, J. G.; Elsevier, C. J., Eds.; Vols. I-III; Wiley-VCH Verlag GmbH & Co. KGaA, **2007**. (b) Wang, D.-S.; Chen, Q.-A.; Lu, S.-M.; Zhou, Y.-G. *Chem. Rev.* **2012**, *112*, 2557. (c) Xie, J.-H.; Zhu, S.-F.; Zhou, Q.-L. *Chem. Soc. Rev.* **2012**, *41*, 4126. (d) Hopmann, K. H.; Bayer, A. *Coord. Chem. Rev.* **2014**, *268*, 59.

(4) Fernández-Pérez, H.; Etayo, P.; Núñez-Rico, J. L.; Balakrishna, B.; Vidal-Ferran, A. *RSC Adv.* **2014,** *4*, 58440.

(5) We have simplified the discussion by indicating only the reagents required for synthesizing the rhodium complexes, whose synthesis has been published (i.e. the antecedents of complexes **4a** and **4b**). The reader is referred to the original publications for the exact reaction conditions employed for a particular P–OP ligand.

(6) (a) Fernández-Pérez, H.; Donald, S. M. A.; Munslow, I. J.; Benet-Buchholz, J.; Maseras, F.; Vidal-Ferran, A. *Chem. Eur. J.* **2010**, *16*, 6495. (b) Panossian, A.; Fernández-Pérez, H.; Popa, D.; Vidal-Ferran, A. *Tetrahedron: Asymmetry* **2010**, *21*, 2281. (c) Etayo, P.; Núñez-Rico, J. L.; Fernández-Pérez, H.; Vidal-Ferran, A. *Chem. Eur. J.* **2011**, *17*, 13978. (d) Etayo, P.; Núñez-Rico, J. L.; Vidal-Ferran, A. *Organometallics* **2011**, *30*, 6718. (e) Núñez-Rico, J. L.; Etayo, P.; Fernández-Pérez, H.; Vidal-Ferran, A. *Adv. Synth. Catal.* **2012**, *354*, 3025. (f) Fernández-Pérez, H.; Benet-Buchholz, J.; Vidal-Ferran, A. *Org. Lett.* **2013**, *15*, 3634. (g) Fernández-Pérez, H.; Benet-Buchholz, J.; Vidal-Ferran, A. *Chem. Eur. J.* **2014**, *20*, 15375. (h) Lao, J. R.; Benet-Buchholz, J.; Vidal-Ferran, A. *Organometallics* **2014**, *33*, 2960.

(7) Lao, J. R.; Fernández-Pérez, H.; Vidal-Ferran, A. *Org. Lett.* **2015,** *17*, 4114.

(8) Manuscript in preperation.

(9) It has been reported that *O*-phosphorylations employing the chlorophosphite derived from ((4*S*,5*S*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(diphenyl-methanol) are not so favored as those involving chlorophosphites from [1,1'-biaryl]-2,2'-diols and require a large excess of base (See for example: Kranich, R.; Eis, K.; Geis, O.; Mühle, S.; Bats, J. W.; Schmalz, H.-G. *Chem. Eur. J.* **2000**, *6*, 2874).

(10) The required chlorophosphite was prepared following the recipe indicated in Scherer, J.; Huttner, G.; Buechner, M.; Bakos, J. *J. Organomet. Chem.* **1996**, *520*, 45.

(11) The required chlorophosphite was prepared following the recipe indicated in Chikkali, S. H.; Bellini, R.; de Bruin, B.; van der Vlugt, J. I.; Reek, J. N. H. *J. Am. Chem. Soc.* **2012**, *134*, 6607.

(12) The required chlorophosphite was prepared following the recipe indicated in Wassenaar, J.; de Bruin, B.; Reek, J. N. H. *Organometallics* **2010**, *29*, 2767.