DOI: 10.1002/adsc.200900621

DiPAMP's Big Brother "*i*-Pr-SMS-Phos" Exhibits Exceptional Features Enhancing Rhodium(I)-Catalyzed Hydrogenation of Olefins

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Received: September 7, 2009; Revised: October 1, 2009; Published online: November 18, 2009

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.200900621.

Abstract: Switching Knowles DiPAMP's {DiPAMP = 1,2-bis[(*o*-anisyl)(phenyl)phosphino]ethane} MeO groups with *i*-PrO ones led to the *i*-Pr-SMS-Phos {*i*-Pr-SMS-Phos = 1,2-bis[(*o*-isopropoxyphenyl)(phenyl)phosphino]ethane} ligand which displayed a boosted catalyst activity coupled with an enhanced enantioselectivity in the rhodium(I)-catalyzed hydrogenation of a wide-range of representative olefinic substrates (dehydro-α-amido acids, itaconates, acrylates, enamides, enol acetates, α,α-diarylethylenes, etc). The rhodium(I)-(*i*-Pr-SMS-Phos) catalytic profile was investigated revealing its structural attributes and robustness, and in contrast to the usual trend, ^{31}P NMR analysis revealed that its methyl (*Z*)-α-acetamidocinnamate (MAC) adduct consisted of a reversed diastereomeric ratio of 1.4:1 in favour of the most reactive diastereomer.

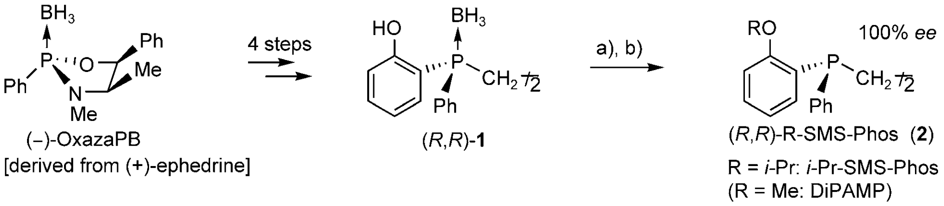
Keywords: asymmetric catalysis; hydrogenation; P ligands; rhodium

The genesis of stereogenic phosphine ligand design for asymmetric catalysis can be traced back to Nobel co-laureate Knowles and co-workers.[1] The success story of their DiPAMP {DiPAMP = 1,2-bis[(*o*-anisyl)-(phenyl)phosphino]ethane} ligand application in the L-DOPA (L-DOPA = L-3,4-dihydroxyphenylalanine) process was the catalyst for the design of C_2-symmetrical diphosphines with a backbone shifted chirality which presented an easier challenge than *P*-chirality.[2] Nevertheless, despite major leaps achieved in the area over the last four decades, a universal solution is lacking due to the structurally diverse plethora of desirable prochiral substrates to undergo transformation.

In our endeavour to prepare a portfolio of new efficient *P*-stereogenic ligands for industrial implementation,[3] we had a strong belief that a golden opportunity still remains in investigating further the pioneering ligand design optimization undertaken by Knowles et al. In particular, during their ligand optimization, Knowles and co-workers prepared and tested a set of *P*-stereogenic 1,2-bis[(*o*-R-phenyl)(phenyl)phos- phino]ethane ligands.[4] Curiously enough, their ultimate conceptual hypothesis was that the *o*-alkoxy groups of their optimum 1,2-bis[(*o*-alkoxyphenyl)(phenyl)-phosphino]ethane model ligand, had to be "normal alkoxys" in order to "provide no significant interference with the steric requirements around the phosphorus atom".[1c,d,f] Noteworthy, Imamoto et al. prepared a set of 1,2-bis[(*o*-alkylphenyl)(phenyl)-phosphino]ethanes, however the overall performance of the new ligands in the Rh(I)-catalyzed hydrogenation of α-acetamidoacrylic acids was not better than that of DiPAMP.[5] Since the work of Knowles, the (*o*-anisyl)(phenyl)phosphino moiety has been systematically appended to new ligand frameworks in order to assess the efficiency of the new *P*-stereogenic designs.[6]

The beneficial effect of our alteration as regards to the incorporation of substituents onto DiPAMP's *P*–*o*-anisyl rings has been shown.[3c] Herein, we report that the alteration of DiPAMP's methyl groups by switching to a higher branched homologue, for example, *i*-Pr, has even a greater impact on the Rh(I)-catalyzed asymmetric hydrogenation of olefins.

We have prepared[3a] the crystalline 1,2-bis[(*o*-hydroxyphenyl)(phenyl)phosphino-*P*-borane]ethane (**1**) (Scheme 1) in 57% overall yield by resorting to an



Scheme 1. *Conditions:* a) *i*-PrI, K_2CO_3, acetone, reflux; b) Et_2NH, 60 °C.

adapted Jugé–Stephan expedient strategy towards phosphines[6c,7]. Their asymmetric route relies upon the sequential displacement of either an (+)- or an (−)-ephedrine auxiliary from the enantiomerically pure 1,3,2-oxazaphospholidine-2-borane complex (oxazaPB) with organolithium reagents. Following a straightforward and high-yielding (94%) functionalization-decomplexation sequence, this key intermediate led to a very large variety of new enantiopure 1,2-bis[(*o*-RO-phenyl)(phenyl)phosphino]ethane ligands (**2**) which we have dubbed "R-SMS-Phos", and wherein R = branched or substituted/functionalized chain.[3a] Thus, the crystalline (*R*,*R*)-1,2-bis[(*o*-*i*-PrO-phenyl)(phenyl)phosphino]ethane [(*R*,*R*)-*i*-Pr-SMS-Phos] ligand was obtained in 54% overall yield from (−)-oxazaPB.

The assessment of the efficiency of *i*-Pr-SMS-Phos in the Rh(I)-catalyzed hydrogenation was first performed on the standard probe substrate methyl (*Z*)-α-acetamidocinnamate (**S6**: MAC). The modification of DiPAMP's MeO groups revealed valuable changes in enantioselectivity and reactivity, as a 99.8% *ee* was obtained in 4 min *vs.* a 94.9% *ee* in 18 min (S/C = 100, 1 bar of H_2, room temperature in MeOH, 100% conversion). Hence, we explored further the potential of *i*-Pr-SMS-Phos on a selected broad spectrum of conventional, more challenging benchmark and new olefinic substrates (Table 1; results correspond to unoptimized conditions).[8,9] The outcome of screening revealed the excellent efficiency and versatility of the Rh(I)-(*i*-Pr-SMS-Phos) catalyst under extremely mild conditions.

Since its conception, DiPAMP performed well in hydrogenation of dehydro-α-amido acids. *i*-Pr-SMS-Phos led to an identical sense of stereoselection, however with 2–5-fold higher reaction rates and superior enantioselectivities for the preparation of a variety of β-substituted- or unsubstituted alanines (hydrogenation products of **S1**–**S10**). Notably, *N*-Boc-alanine was obtained with >99.9% *ee*, and a same magnitude of reaction rate coupled with a high enantioselectivity was maintained for substrates containing coordinating groups such as 3-pyridyl (**S7**) or 4-cyanophenyl (**S8**). Also, β,β-disubstituted dehydro-α-amido acids **S9** and **S10**, which present a difficult challenge, were similarly reduced under 3 bar of H_2 in 5 min with 98.7% and 99.2% *ee*, respectively, expanding the prospects of this catalyst. However, (*Z*)- and (*E*)-dehydro-β-methyl-β-amido acids (**S11** and **S12**) were reduced with 82.1% and 90.4% *ee*, respectively. Interestingly, hydrogenation of MAC under 5 bar H_2 at room temperature with an S/C = 10000 led to 98.5% *ee* with full conversion in 3 h; also, operating at 0.5 M MAC concentration did not affect the reaction rate or *ee*.

High enantioselectivities (97.4–99.0% *ee*) were also attained with 2-methylidene-succinamic acid (**S14**), itaconic acid (**S13**: IA) and its dimethyl ester (**S15**: DMI). Noteworthy, for itaconic acid, a 98.7% *ee* with 100% conversion was attained in 4 min.

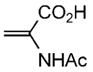
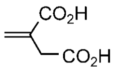
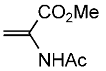
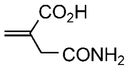
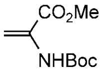
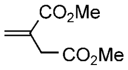
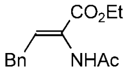
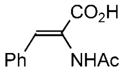
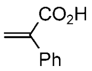
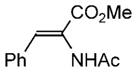
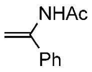
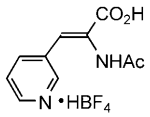
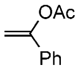
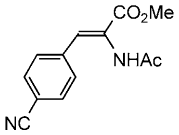
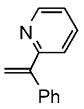
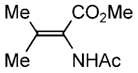
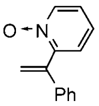
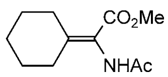
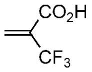
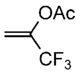
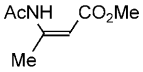
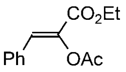
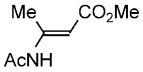
α-Substituted styrenes and trifluoromethylethylenes are interesting candidates for asymmetric hydrogenation and present a stiff challenge. *i*-Pr-SMS-Phos displayed exceptionally high enantioselectivities and reaction rates in the Rh(I)-catalyzed hydrogenation of α-carboxy- (**S16**), α-acetamido- (**S17**), and α-acetoxy-styrenes (**S18**). Namely, atropic acid (**S16**) was reduced under 10 bar of H_2 with a respectable 89.1% *ee* in the presence of dicyclohexylamine (79.3% *ee* in its absence). Also, by analogy to atropic acid, hydrogenation of α-trifluoromethylacrylic acid (**S21**) furnished a high *ee* (94.5%) with the same sense of stereoselection.[10]

Interestingly enough, new α,α-diarylethylene substrates capable of a three-pronged binding such as α-(2-pyridyl)- (**S19**) and α-(2-pyridyl-*N*-oxide)-styrenes (**S20**), were hydrogenated with 84.6 and 97.4% *ee*, respectively, with a protracted reaction time in the case of **S19**. Hence, the incidence on hydrogenation of the Rh···substrate chelate ring size and the coordination strength of the heteroatoms involved are manifested.

Moreover, enol acetates **S22** and **S23** were hydrogenated with exceptionally high enantioselectivities as 94.5 and 99.6% *ee*s were obtained, respectively.

X-ray of the catalyst precursor {Rh[(R,R)-i-Pr-SMS-Phos)(NBD)]}BF$_4$: The X-ray diffraction analysis of this complex revealed a pronounced dissymmetry of this C_2-symmetrical ligand (Figure 1).[11] It showed the 5-membered chelate ring in an envelope λ-conformation where one backbone CH_2 is at the flap of the envelope, and the other CH_2 is situated nearly in plane. Also, the bulky *P*–*o*-*i*-PrOPh and the *P*–Ph at the fold of the envelope occupy an equatorial (face/in) and an axial (edge) position, respectively, while the other *P*–*o*-*i*-PrOPh is in a face/out orienta-

Table 1. [Rh(*i*-Pr-SMS-Phos)(MeOH)$_2$]BF$_4$ catalyzed hydrogenation of miscellaneous olefinic model substrates **S1**–**S23**.[a]

Olefin		*t* [min]	*ee* [%]	Olefin		*t* [min]	*ee* [%]
	**S1**	5	98.6		**S13** (IA)	4	98.7
	**S2** (MAA)	8	99.4		**S14** **S14**[d]	3 6	99.0 98.4
	**S3**	5	>99.9		**S15** (DMI)	5	97.4
	**S4**	3	98.8		**S15**[b]	13	97.8
	**S5** (AAC)	5	99.6		**S16**	3 h	79.3
	**S6** (MAC)	4,	99.7		**S16**[e]	3 h	89.1
	S6[b]	15	98.9		**S17**	3	97.8
	S6[c]	3 h	98.5		**S17**[b]	15	97.7
	**S7**	5	97.3		**S18**	45	92.8
	**S8**	3	99.1		**S19**	16 h	84.6
	**S9**	5	98.7		**S20**	10	97.4
	**S10**	5	99.2		**S21**[e]	3 h	94.5
	S10[b]	30	99.1		**S22**	15	96.1
	**S11** (*Z*-MAB)	20	82.1		**S23**	16 h	99.6
	**S12** (*E*-MAB)	90	90.4				

[a] The catalyst was prepared *in situ* from [Rh(NBD)$_2$]BF$_4$. Runs were carried out under 1 bar of H$_2$ (3 bar for **S9**, **S10** and **S19**, and 10 bar for **S16** and **S21**) at room temperature (50 °C for **S20**) in MeOH (0.5 mmol of substrate in 7.5 mL MeOH) with an S/C = 100 (S/C = 500 for **S1**, and 1000 for **S2**) for the time indicated (100% conversion) if not stated otherwise. Typical isolated yields were >90%. The *ee* values were determined by: chiral GC for **S1**–**S18** (prior to analysis carboxylic groups of hydrogenation products of **S1**, **S5**, **S7**, **S13**, **S14**, and **S16** were esterified with TMSCHN$_2$); chiral HPLC for **S19**, **S20**, and **S23** (hydrogenation product of **S19** was analyzed as its *N*-oxide); ^{19}F NMR [in the presence of (+)-ephedrine] and ^{1}H NMR [in the presence of (+)-Pr(hfc)$_3$] for hydrogenation products of **S21** and **S22**, respectively. With (*R*,*R*)-*i*-Pr-SMS-Phos, *S*-configured products were obtained except with **S13**, **S14**, **S15**, and **S21**.

[b] S/C = 500.

[c] S/C = 10000, under 5 bar of H$_2$ and using 2 mmol of **S6**, (*S*)-*N*-acetylphenylalanine methyl ester isolated in 97% yield.

[d] S/C = 1000.

[e] Cy$_2$NH (1.1 equiv.) was added. With Et$_3$N, 87.8% *ee* was obtained for **S16**.

tion.[12a] The aryls are in an alternating face-edge disposition in accordance with the averaged torsion angles $\gamma_{1\text{-}4}$ [Rh–P–C$_{ipso}$–C$_{ortho}$][12b]. By contrast, the aryls in {Rh[(*S*,*S*)-DiPAMP](NBD)}BF$_4$ (which has a half chair δ-conformation) are in an almost symmetrical orientation with the *P*–Ph and the *P*–*o*-MeOPh

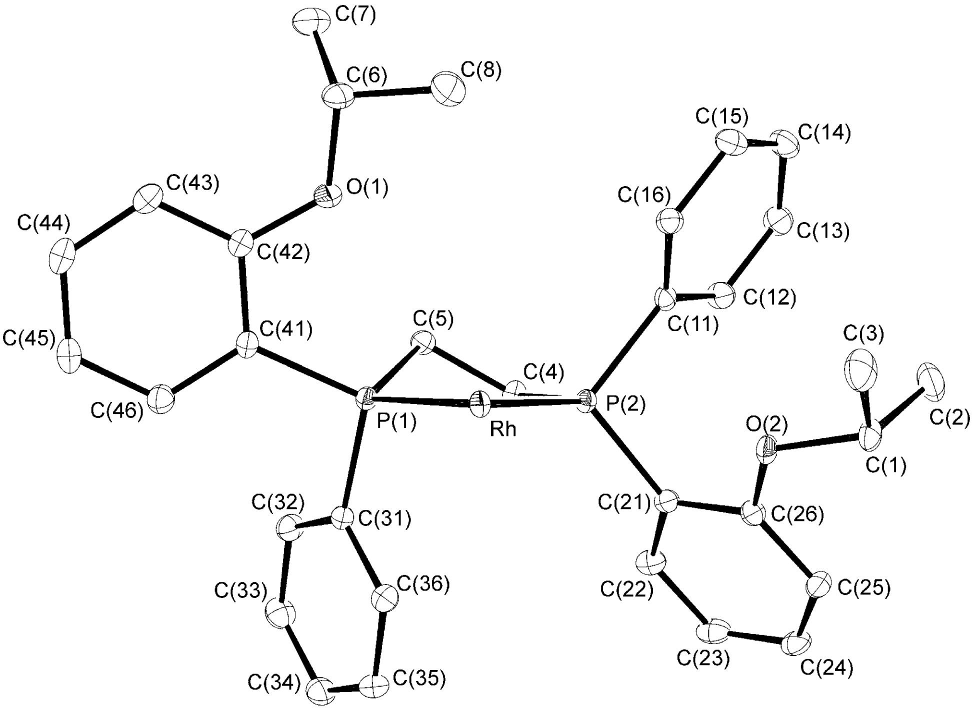


Figure 1. ORTEP drawing of [Rh((*R*,*R*)-*i*-Pr-SMS-Phos)(NDB)]BF_4 complex in elevation view into the coordination-plane. Coordinated NBD (NBD = 2,5-norbornadiene) and counter-anion (BF_4^-) are omitted for clarity. Relevant bond lengths or interatomic distances [Å] and angles [deg]: Rh–P(1) 2.2758(6), Rh–P(2) 2.3218(6), Rh···O(1) 3.667(2), Rh···O(2) 3.888(2), P(1)–Rh–P(2) 83.17(2) (bite angle), $\gamma_1 = 65.0$, $\gamma_2 = 5.5$, $\gamma_3 = -73.9$, $\gamma_4 = 2.0$ (for aryls going from top left to top right).

Table 2. Solvent dependence.[a]

Solvent	*t* [min]	*ee* [%]
MeOH	3–4	99.7
EtOH	4	99.5
i-PrOH	5	98.6
MeCN	120	86.7
EtOAc	4	99.2
Acetone	3–4	99.7
THF	6	97.6
CH_2Cl_2	6	98.7
$CHCl_3$	8	99.4
Toluene	15	97.9

[a] Crystalline [Rh(*i*-Pr-SMS-Phos)(NBD)]BF_4 catalyst precursor was used.

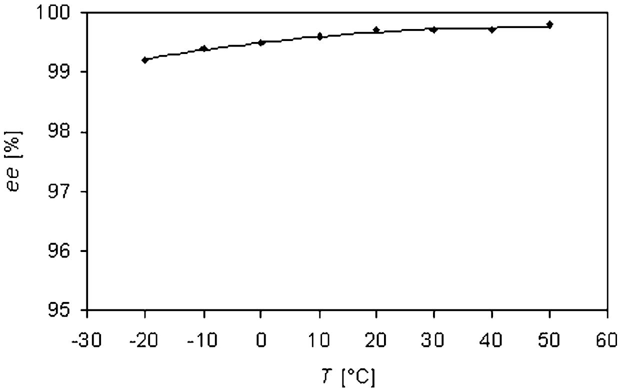


Figure 2. Temperature effect.

groups in a respective alternating edge-face/out disposition.[13]

Establishment of the catalytic profile of Rh[(R,R)-i-Pr-SMS-Phos]: We have investigated the susceptibility of the [Rh(*i*-Pr-SMS-Phos)]$^+$-catalyzed hydrogenation of MAC (**S6**) to reaction parameters (Table 2 and Figure 2 and Figure 3; for the remaining reaction parameters, see Table 1). A high *ee* in the range of 97.6–99.7% was maintained in various reaction media. However, the binding solvent acetonitrile led to a 13% decrease in *ee* and to a protracted reaction time. In toluene, the reaction time was increased by a factor of 3 to allow full conversion.[14] Performing the hydrogenation with *i*-Pr-SMS-Phos at temperatures in the range of −20 to 50 °C demonstrated an increase in the *ee* with increasing temperature. Thus, a 99.8% *ee* with full conversion within 2 min was reached at 50 °C compared to 99.2% *ee* in 60 min at −20 °C.[15] In general, the H_2 pressure markedly affects the hydrogenation results of MAC. However, with *i*-Pr-SMS-Phos a 98.8% *ee* was maintained up to 10 bar of H_2, and it only dropped to 94.6% at 40 bar of H_2.

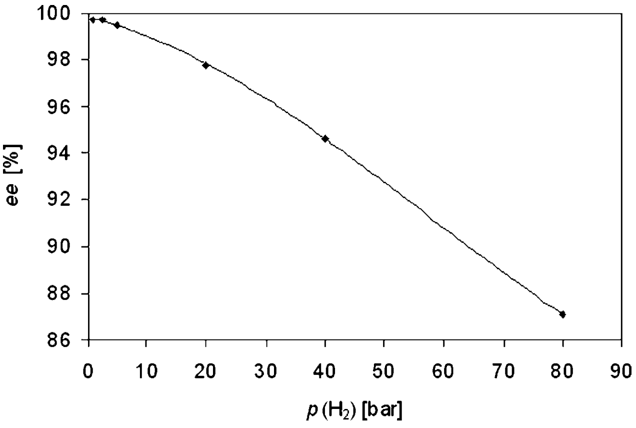


Figure 3. Pressure effect.

^{31}P NMR study of the {Rh[(R,R)-i-Pr-SMS-Phos]-(MAC)]BF$_4$ adduct complex: Monitoring the evolution of [Rh(*i*-Pr-SMS-Phos)(NBD)]BF$_4$ throughout the various stages of its transformation was carried out by ^{31}P NMR. Thus, the hydrogenation of NBD in [Rh(*i*-Pr-SMS-Phos)(NBD)]BF$_4$ in MeOH at room temperature led to the disappearance of the doublet at $\delta = +52.4$ ppm (d, $J = 158$ Hz) and the appearance of a doublet at $\delta = +81.0$ ppm (d, $J = 206$ Hz) corresponding to the formation of the [Rh(*i*-Pr-SMS-Phos)-(MeOH)$_2$]BF$_4$ solvate complex. Upon admixing this solution and MAC (8 equiv.) in MeOH at room temperature, an identical pattern of signals corresponding to the formation of two [Rh(*i*-Pr-SMS-Phos)-(MAC)]BF$_4$ diastereomers was obtained, reminiscent of the observed one[16] with [Rh(DiPAMP)(MAC)]$^+$ (Figure 4). The ^{31}P NMR signals of the minor diastereomer resonate at $\delta = +53.0$ [dd, $J(^{103}\mathrm{Rh},^{31}\mathrm{P}) = 152$ Hz, $J(^{31}\mathrm{P},^{31}\mathrm{P}) = 37$ Hz], $+72.7$ [dd, $J(^{103}\mathrm{Rh},^{31}\mathrm{P}) = 162$ Hz, $J(^{31}\mathrm{P},^{31}\mathrm{P}) = 37$ Hz], and the ^{31}P NMR signals of the major diastereomer resonate at $\delta = +61.2$ [dd, $J(^{103}\mathrm{Rh},^{31}\mathrm{P}) = 158$ Hz, $J(^{31}\mathrm{P},^{31}\mathrm{P}) = 35$ Hz], $+69.4$ [br dd, $J(^{103}\mathrm{Rh},^{31}\mathrm{P}) = 158$ Hz, $J(^{31}\mathrm{P},^{31}\mathrm{P}) = 35$ Hz]. However, two major differences are noticeable: (1) the signals corresponding to the P_{trans} to the amide carbonyl of the major diastereomer are broadened, and (2) the ratio of diastereomers is 1.4 in favour of the most reactive one towards H_2. This was confirmed by equilibrating the mixture at −50 °C, H_2 was partially admitted at −40 to −50 °C in the NMR tube and ^{31}P NMR spectrum was recorded at −50 °C. The latter experiment unambiguously demonstrated the disappearance of the "major diastereomer" which otherwise corresponds at the placement in ^{31}P NMR of the "minor diastereomer" with DiPAMP as ligand. In the present case using *i*-Pr-SMS-Phos as ligand, a reversed ratio of diastereomers is obtained to the traditional one.

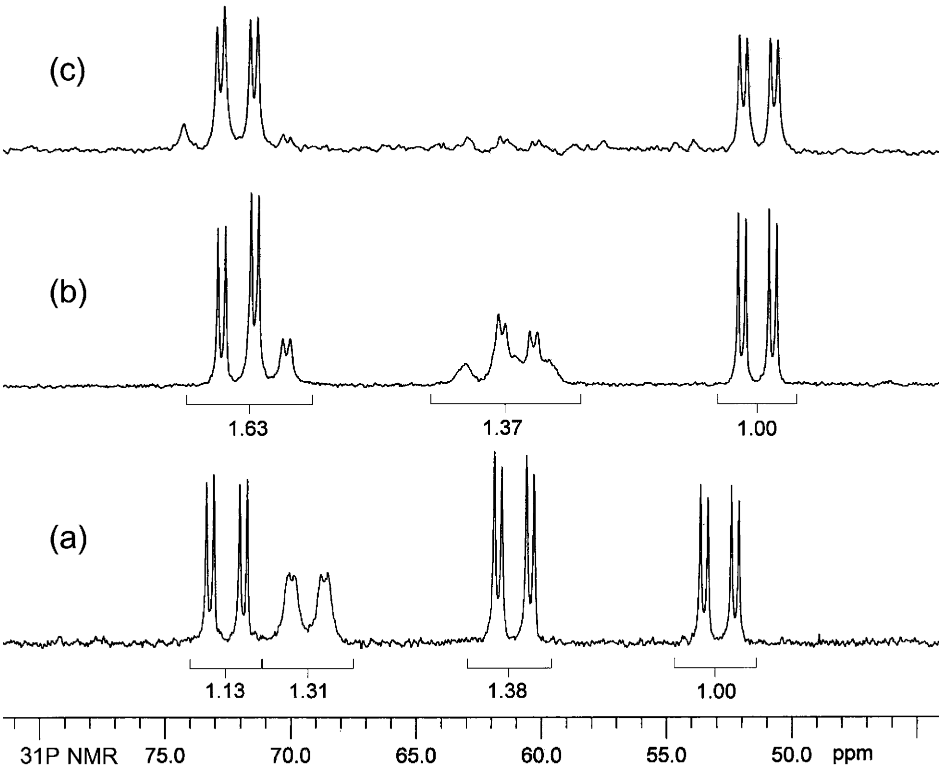


Figure 4. Plots of ^{31}P NMR spectra showing (a) equilibrated [Rh[(*R*,*R*)-*i*-Pr-SMS-Phos)(MAC)]BF$_4$ diastereomers: minor (at +53.0 and +72.7 ppm) and major (at +61.2 and +69.4 ppm) at room temperature, (b) at −50 °C, and (c) subsequent partial hydrogenation at −40 to −50 °C and recording the spectrum at −50 °C.

This is an unprecedented event in Rh(I)-catalyzed asymmetric hydrogenation with diphosphines where typically the most reactive diastereomer (dominating the selectivity) is present in a considerably lower amount than the less reactive diastereomer.[17] This affects the enantioselectivity which is regulated by the relative reactivities and concentration ratio of the diastereomeric substrate···Rh complex intermediates.[18]

In summary, we have prepared with high overall yield (94%) enantiopure *P*-stereogenic *i*-Pr-SMS-Phos in 2-steps from 1,2-bis[(*o*-hydroxyphenyl)(phenyl)-phosphino-*P*-borane]ethane. The seemingly trivial and déjà vu alteration of the DiPAMP's MeO groups carried out by Knowles and co-workers, turned out still to offer interesting perspectives. The present alteration culminated in an efficient ligand which boosted reaction rate by several times and increased enantioselectivities in the Rh(I)-catalyzed asymmetric hydrogenation of a wide-range of dehydro-α-amido acids, itaconates, acrylates, enamides, enol acetates, and α,α-diarylethylenes. Furthermore, the study outcome of the catalytic profile of Rh(I)-(*i*-Pr-SMS-Phos) revealed the structural attributes and robustness of this catalyst system. Ongoing studies to gain insight into the hydrogenation mechanism pathway will be forthcoming.

Experimental Section

General Remarks

All operations were conducted under N_2 or Ar atmosphere using anhydrous and degassed solvents. ^{1}H (300 MHz, internal Me_4Si), ^{13}C (75 MHz, internal $CDCl_3$), and ^{31}P NMR (120 MHz, external 85% H_3PO_4) were recorded for solutions in $CDCl_3$.

($R_P R_P$)-1,2-Bis[(2-isopropoxyphenyl)(phenyl)phosphino-*P*-borane]ethane

A mixture of ($R_P R_P$)-1,2-bis[(2-hydroxyphenyl)(phenyl)-phosphino-*P*-borane]ethane (**1**)[3a] (458 mg, 1 mmol), K_2CO_3 (553 mg, 4 mmol) and 2-iodopropane (0.68 g, 0.40 mL, 4.0 mmol) in acetone (2 mL) was refluxed overnight. The mixture was concentrated, taken with CH_2Cl_2, filtered through a pad of silica gel, concentrated and recrystallized from hexane/CH_2Cl_2 affording colourless crystals; yield: 525 mg (97%): mp 159–161 °C; $R_f = 0.62$ (toluene/EtOAc 9:1); $[\alpha]_D^{25}$: +102.0 deg cm^3 g^{-1} dm^{-1} (c 1.0 g dcL^{-1} in $CHCl_3$); ^{1}H NMR: $\delta = 0.30$–1.75 (br m, 6H, 2 BH_3), 0.91 and 1.16 (2d, $J = 6.1$ Hz, 12H, 4 Me), 2.65 (m, 4H, 2 CH_2), 4.44 (sept, $J = 6.0$ Hz, 2H, 2 CH), 6.75 (m, 2H, Ar-H), 6.97 (m, 2H, Ar-H), 7.39 (m, 8H, Ar-H), 7.64 (m, 4H, Ar-H), 7.90 (m, 2H, Ar-H); ^{13}C NMR: $\delta = 17.4$ (m), 20.8, 21.4, 69.7, 111.6, 115.7 (d, $J_{C,P} = 53$ Hz), 120.1 (m), 128.2 (m), 129.7 (d, $J_{C,P} = 59$ Hz), 130.4, 131.7 (m), 133.6, 136.60 (m), 159.2; ^{31}P NMR: $\delta = +18.3$ (br m); MS (FAB): $m/z = 541$ [$M^+ - $H] (19%); anal. calcd for $C_{32}H_{42}B_2O_2P_2$: C 70.88, H 7.81; found: C 71.10, H 8.10.

($R_P R_P$)-1,2-Bis[(2-isopropoxyphenyl)(phenyl)phosphino]ethane [($R_P R_P$)-*i*-Pr-SMS-Phos]

($R_P R_P$)-1,2-Bis[(2-isopropoxyphenyl)(phenyl)phosphino-*P*-borane]ethane (0.41 g, 0.75 mmol) in Et_2NH (7.5 mL) was heated at 55–60 °C for 3 h under an inert atmosphere. After concentration, purification on silica gel eluting with toluene, concentration and recrystallization from hexane/CH_2Cl_2 under inert atmosphere, *i*Pr-SMS-Phos was obtained as colourless crystals; yield: 375 mg (97%): mp 72–74 °C; R_f 0.58 (toluene); $[\alpha]_D^{25}$: −57.8 deg cm^3 g^{-1} dm^{-1} (c 1.0 g dcL^{-1} in $CHCl_3$); ^{1}H NMR: $\delta = 1.03$ and 1.17 (2d, $J = 6.0$ Hz, 12H, 4 Me), 1.95 and 2.31 (2 m, 4H, 2 CH_2), 4.47 (sept, $J = 6.0$ Hz, 2H, 2 CH), 6.72–6.85 (m, 4H, Ar-H), 7.04 (m, 2H, Ar-H), 7.15–7.38 (m, 12H, Ar-H); ^{13}C NMR: $\delta = 21.5$, 21.7, 22.0 (d, $J_{C,P} = 4$ Hz), 69.7, 111.9, 120.2, 127.7 (m), 128.1 (m), 128.4, 129.6, 132.4 (m), 133.4 (m), 137.8 (m), 159.1 (m); ^{31}P NMR: $\delta = -19.1$ (s); MS (FAB): $m/z = 515$ [$M^+ + $H] (100%); HRMS (EI): $m/z = 514.220$, calcd. for $C_{32}H_{36}O_2P_2$ [M^+]: 514.219; anal. calcd. for $C_{32}H_{36}O_2P_2$: C 74.69, H 7.05; found: C 74.82, H 7.19.

{Rh[(*R*,*R*)-*i*-Pr-SMS-Phos](NBD)}BF_4 Complex

To a solution of (*R*,*R*)-*i*-Pr-SMS-Phos (257 mg, 0.5 mmol) in MeOH (2 mL) was added in one portion $[RhCl(NBD)]_2$ (115 mg, 0.25 mmol) at room temperature. The resulting mixture was left to stir for 1 h affording a deep red solution. Subsequently, a solution of $NaBF_4$ (82 mg, 0.75 mmol) in H_2O (1 mL) was slowly added. The precipitated fine orange powder was filtered, rinsed with H_2O (5 mL), and dried in vacuum; yield: 360 mg (90%). The complex was recrystallized from EtOH (5 mL) affording red crystals; yield: 320 mg (80%); mp 227–229 °C; ^{1}H NMR: $\delta = 0.87$ and 0.91 (2d, $J = 6.1$ Hz, 12H, 4 Me), 1.78 (s, 2H, $CHCH_2CH$), 2.21–2.73 (m, 4H, CH_2CH_2), 4.17 (m, 2H, $CHCH_2$), 4.44 (sept, $J = 6.1$ Hz, 2H, 2 CH), 5.19 (m, 2H, CH=CH), 5.31 (m, 2H, CH=CH), 6.88 (m, 2H, Ar-H), 7.15 (m, 2H, Ar-H), 7.34–7.57 (m, 12H, Ar-H), 7.86 (m, 2H, Ar-H); ^{13}C NMR: $\delta =$ 21.0, 21.4, 25.1 (d, $J_{C,P} = 2$ Hz), 25.4, 25.7 (d, $J_{C,P} = 2$ Hz), 55.3, 70.2, 71.0, 87.9 (m), 91.4 (m), 112.7, 117.0 (m), 120.9 (m), 129.2 (m), 130.7, 130.8 (m), 131.5 (m), 134.1, 136.4 (m), 158.3; ^{31}P NMR: $\delta = +52.4$ [d, J(P,Rh) = 158 Hz].

In situ Preparation of [Rh((*R*,*R*)-*i*-Pr-SMS-Phos)$(MeOH)_2$]BF_4 catalyst

To a solution of $[Rh(NBD)_2]BF_4$ (2.4 mg, 6.3 μmol) in MeOH (0.5 mL), a solution of (*R*,*R*)-*i*-Pr-SMS-Phos (2.6 mg, 5.0 μmol) in MeOH (0.5 mL) was added dropwise at room temperature. The resulting solution was hydrogenated under 1 bar of H_2 for *ca.* 15 min. Elimination of metallic rhodium by filtration through a No. 3 sintered-glass filter afforded a clear brown solution of [Rh((*R*,*R*)-*i*-Pr-SMS-Phos)-$(MeOH)_2$]BF_4. ^{31}P NMR: $\delta = +81.0$ [d, J(P,Rh) = 206 Hz].

Hydrogenation Procedure for the Substrates in Table 1

To a solution of the olefin (0.5 mmol) in MeOH (7 mL), three freeze-pump-thaw cycles were applied and the system was filled with Ar. Then to this solution was added under argon a solution of the preformed [Rh(*i*-Pr-SMS-Phos)-

$(MeOH)_2]BF_4$ catalyst (for substrate/catalyst molar ratio, see Table 1) in MeOH (prepared *in situ* as above). A vacuum was applied to the system then it was backfilled with H_2. The mixture was stirred at room temperature under 1–10 bar of H_2. The progress of the hydrogenation was monitored by the diminution of the volume of the closed reaction system at 1 bar (until H_2 uptake ceased) and the colour change of the solution. The *ee* values were determined by: chiral GC for **S1**–**S18** (prior to analysis carboxylic groups of hydrogenation products of **S1**, **S5**, **S7**, **S13**, **S14**, and **S16** were esterified with $TMSCHN_2$); chiral HPLC for **S19**, **S20**, and **S23** (hydrogenation product of **S19** was analyzed as its *N*-oxide); ^{19}F NMR [in the presence of (+)-ephedrine] and ^{1}H NMR [in the presence of $(+)\text{-}Pr(hfc)_3$] for hydrogenation products of **S21** and **S22**, respectively. Absolute configurations were assigned by comparison of the optical rotations of the isolated products with the literature data.

Acknowledgements

This work was supported by the Ministry of Higher Education, Science, and Technology of the Republic of Slovenia (grants P1-242 and J1-9806), and by the Ministry of National Education, Research, and Technology of France (grant 00P141) to PhosPhoenix SARL. We thank Dr. Barbara Modec, University of Ljubljana, for the X-ray crystal structure analysis.

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