Catalysis Science & Technology

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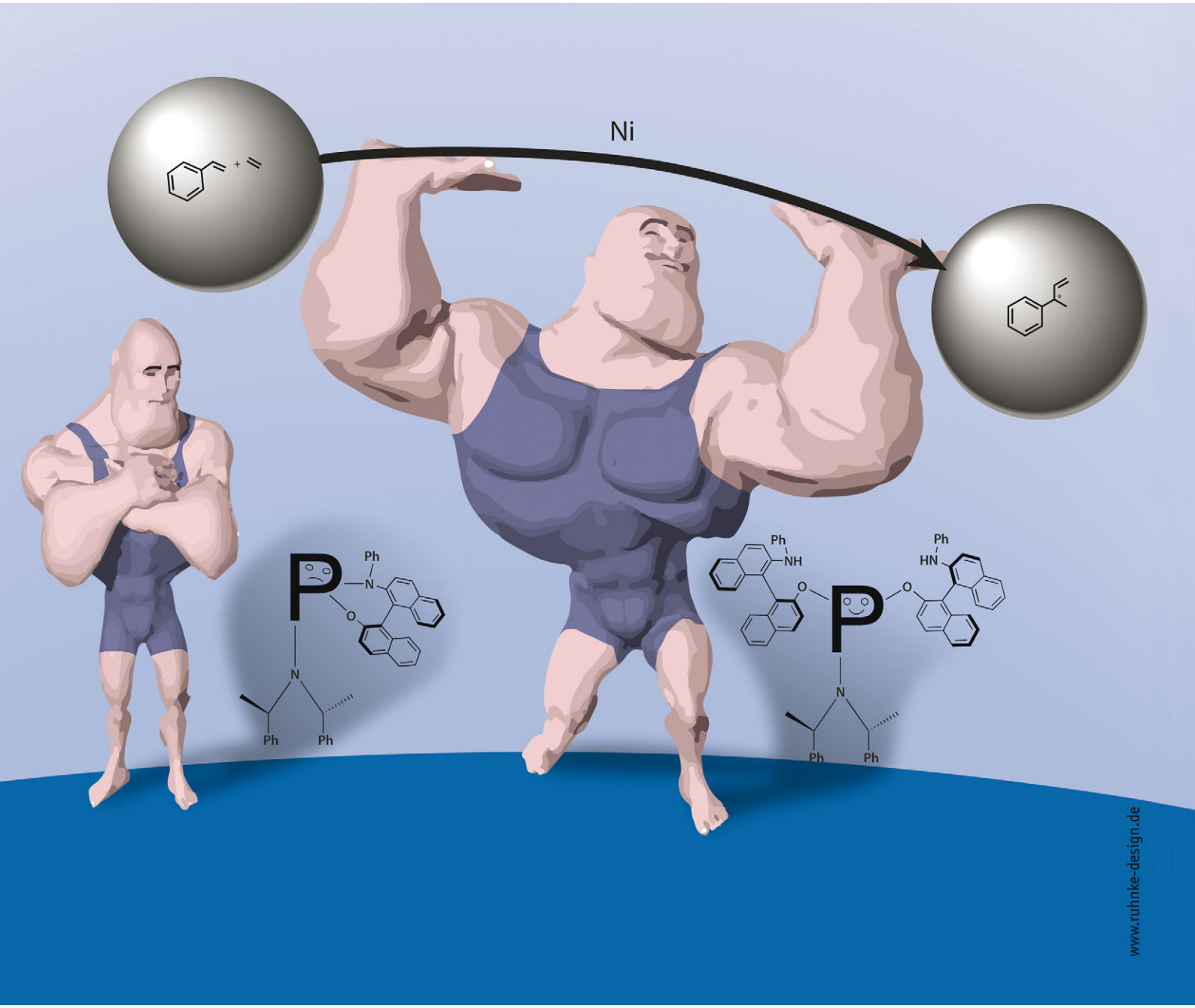
Volume 3 | Number 3 | March 2013 | Pages 529–820



ISSN 2044-4753

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Cite this: *Catal. Sci. Technol.*, 2013, **3**, 589

NOBIN-based phosphoramidite and phosphorodiamidite ligands and their use in asymmetric nickel-catalysed hydrovinylation†

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Received 19th September 2012,
Accepted 30th October 2012

DOI: 10.1039/c2cy20657a

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Phosphoramidite and P-stereogenic phosphorodiamidite ligands derived from (S_a)-2-phenylamino-2′-hydroxy-1,1′-binaphthyl (*N*-Ph-NOBIN) and bis(1-phenyl-ethyl)amine were synthesised, fully characterised, and the absolute configuration of the stereogenic phosphorus atoms was assigned. The phosphoramidite ligand **L2** features three non-bridged substituents at phosphorus comprising the bis(1-phenylethyl)amine and two NOBIN moieties. The NOBIN units are bound to the phosphorus through the oxygen atoms with two pendant nitrogen atoms. In the Ni-catalysed hydrovinylation of styrene no conversion was observed with the phosphorodiamidites, while the phosphoramidite ligands led to active catalysts with a marked co-operative effect on selectivities. Whereas the racemic product was obtained with the (S_a,S_a,S_C,S_C) diastereomer, the (S_a,S_a,R_C,R_C) diastereomer proved to be one of the best ligands for this reaction, leading to almost perfect selectivity and ees of up to 91%.

Introduction

Chiral phosphorus(III) compounds in which the donor atom is surrounded by heteroatoms are finding increasing application as ligands for transition metal catalysed reactions.[1] Their synthesis is modular and suitable for automation allowing for the creation of ligand libraries to rapidly assess the optimum structure for a given application.[2] In particular, BINOL-based (BINOL = 1,1′-binaphthyl-2,2′-diol) phosphoramidites are excellent chiral auxiliaries for a variety of asymmetric metal-catalysed reactions when used as monodentate ligands[3] as well as in combination with a second donor group within the same molecule[4] or with a second ligand.[5] More recently, several groups synthesised phosphorous triamides based on variously substituted 2,2′-diamino-1,1′-binaphthyl backbones[6–8] and applied them in catalysis, albeit without reaching the efficiency level of the related phosphoramidites. A small number of monodentate phosphorodiamidite (diamido phosphite) ligands have also been synthesised, either from diamines and an alcohol or amino alcohols and amines.[1] Their use in catalysis is far less investigated.[9] In all cases, the bidentate units bind to phosphorus in a ''chelating-type'' fashion, resulting in the cyclic structure of type **A** (Fig. 1).

Despite the close similarity of the atropoisomeric amino-alcohol NOBIN (NOBIN = 2′-amino-1,1′-binaphthyl-2-ol)[10] to BINOL, no corresponding phosphorodiamidite ligands have been reported yet.[11] Intrigued by this structural variation, we set to synthesise phosphorodiamidite ligands from the NOBIN moiety and the bis(1-phenylethyl)amine, a very successful chiral synthon for phosphoramidite ligands.[12,13]

We describe here the synthesis of P-stereogenic phosphorodiamidite derived from (S_a)-2′-(phenylamino)-1,1′-binaphthyl-2-ol and both enantiomers of bis(1-phenylethyl)amine. In addition to the expected phosphorodiamidite of structure **A**, the non-cyclic

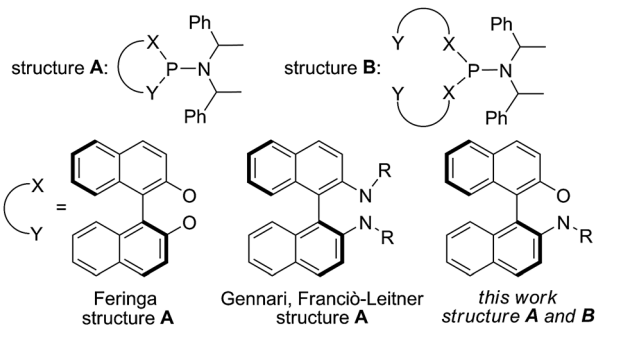

Fig. 1 Phosphoramidite, phosphorous triamide and phosphorodiamidite with related structures.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c2cy20657a

phosphoramidite structure **B** (Fig. 1) could be obtained in excellent yields and proved the preferred arrangement in asymmetric hydrovinylation.

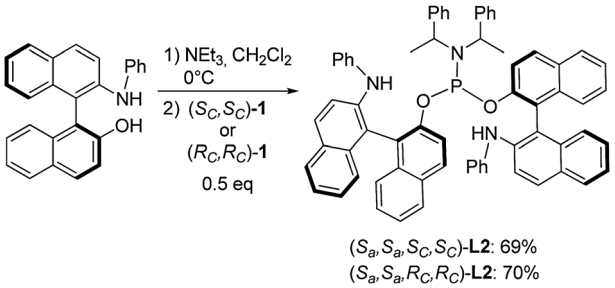
Results and discussion

Ligand synthesis

The synthesis of the phosphorodiamidites of type **A** was carried out using a protocol established for the phosphoramidites[14] or phosphorous triamide[7,8] congeners (Scheme 1). Adding an equimolar amount of (S_a)-*N*-Ph-NOBIN to enantiopure 1,1-dichloro-*N*,*N*-bis(1-phenylethyl)phosphinamine (S_C,S_C)-**1** at 0 °C in CH_2Cl_2 in the presence of NEt_3 resulted in the formation of two P-containing products, which could be separated through column chromatography and isolated in pure form (*vide infra*). The major product (45% yield), displaying in the $^{31}P\{^1H\}$-NMR-spectrum a singlet at δ = 142.72 ppm, corresponds to the anticipated phosphorodiamidite (S_a,S_C,S_C,R_P)-**L1** and was obtained as a single diastereomer. A similar outcome was observed by the reaction of (S_a)-*N*-Ph-NOBIN with (R_C,R_C)-**1**. Again, a single phosphorodiamidite diastereomer (S_a,R_C,R_C,R_P)-**L1** was isolated in 35% yield ($^{31}P\{^1H\}$-NMR: singlet, δ = 135.00 ppm). These results indicate that the formation of one diastereomer of type **A** with NOBIN is kinetically and/or thermodynamically highly preferred over the other.[15]

The assignment of the absolute configuration of the stereogenic phosphorus atom[16] was accomplished by computational methods and corroborated by NMR spectroscopy. The conformational minima for both diastereomeric pairs were calculated *via* conformational searches at the PM3 level followed by geometry optimisation through DFT calculation (see ESI†). The calculation showed that for both phosphorodiamidites (S_a,S_C,S_C)-**L1** and (S_a,R_C,R_C)-**L1** the *R* configuration at the phosphorus is strongly favoured with a ΔG of 8.7 and 5.2 kcal mol^{-1} for the pairs (S_a,S_C,S_C,R_P)–(S_a,S_C,S_C,S_P) and (S_a,R_C,R_C,R_P)–(S_a,R_C,R_C,S_P), respectively. These findings were confirmed in solution by 2D NOE experiments, where predicted interactions specific for R_P-diastereomers were actually found (see ESI†).

The minor products isolated in 12–13% yield from the reactions described above showed in the $^{31}P\{^1H\}$-NMR-spectra a singlet at δ = 141.17 and 141.37 ppm for the compound obtained from (S_a)-*N*-Ph-NOBIN with (S_C,S_C)-**1** and (R_C,R_C)-**1**, respectively. ^1H and ^{13}C NMR spectroscopy as well as mass analysis revealed these compounds as phosphoramidites of type **B** comprising a bis(1-phenyl-ethyl)amine and two (S_a)-*N*-Ph-NOBIN moieties, which are bound to the phosphorus through the oxygen atoms. The latter connectivity could be unequivocally confirmed on the basis of ^{13}C NMR: the quaternary carbons next to the oxygen atoms appear as doublets at δ = 150.59 ($J_{^{13}C-^{31}P}$ = 6.3 Hz) and 150.43 ($J_{^{13}C-^{31}P}$ = 7.6 Hz) ppm for (S_a,S_a,S_C,S_C)-**L2** and at δ = 150.84 ($J_{^{13}C-^{31}P}$ = 8.6 Hz) and 150.30 ($J_{^{13}C-^{31}P}$ = 1.8 Hz) ppm for (S_a,S_a,R_C,R_C)-**L2**, respectively, as the most downfield signals. In contrast, in both diastereomers the quaternary carbon next to the nitrogen atoms does not show any phosphorus-coupling.



Scheme 2 Phosphoramidite synthesis.

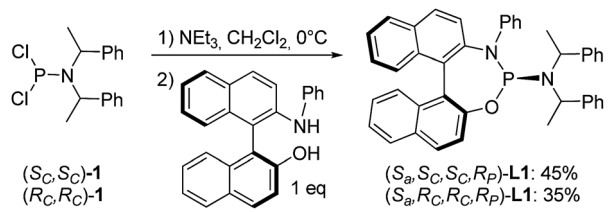
Based on this unexpected observation, the reaction conditions were adjusted in order to favour the formation of type **B** structures. Thus, the synthesis was carried out using a (S_a)-*N*-Ph-NOBIN/**1** molar ratio of 2 : 1, the addition sequence inverted (*i.e.* the PCl_2-compound **1** was added to NOBIN), and the concentration increased by a factor of 10 to facilitate the inter- over the intra-molecular addition (Scheme 2). Indeed, phosphoramidites (S_a,S_a,S_C,S_C)- and (S_a,S_a,R_C,R_C)-**L2** formed as the only P-containing species and could be isolated in 69% and 70% yields, respectively.

Ni-catalysed asymmetric hydrovinylation

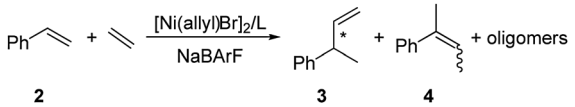
The diastereomeric pairs of novel ligand structures **L1** and **L2** were applied in the Ni-catalysed hydrovinylation of styrene (Scheme 3),[17] where BINOL-based phosphoramidites are the benchmark ligands.[18]

Both (S_a,R_C,R_C,R_P)-**L1** and (S_a,S_C,S_C,R_P)-**L1** did not form an active Ni-catalyst (Table 1, entries 1 and 2). This result is surprising as the structure of the phosphorodiamidites **L1** lies "in-between" that of the Feringa phosphoramidite and that of the phosphorous triamides based on the 2,2′-diamino-1,1′-binaphthyl backbone, which led to high conversions and enantioselectivities of 91% and 40% ee, respectively, under similar reaction conditions.[8,18a]

Most intriguingly, the use of the phosphoramidite (S_a,S_a,S_C,S_C)-**L2** resulted in an active but unselective hydrovinylation catalyst and the target chiral product 3-phenyl-but-1-ene **3** was obtained as a racemic mixture (entry 3). The other diastereomer (S_a,S_a,R_C,R_C)-**L2** was more active as judged from the



Scheme 1 Phosphorodiamidite synthesis.



Scheme 3 Hydrovinylation of styrene.

Table 1 Ni-catalysed hydrovinylation of styrene

Entry	Ligand	2/[Ni]	T (°C)	t (h)	Conversion (%)	Selectivity[a] (%) 3	4	Olig.	ee (%)
1	(S_a,S_C,S_C,R_P)-**L1**	500	20	1	4	—	—	—	—
2	(S_a,R_C,R_C,R_P)-**L1**	500	20	1	4	—	—	—	—
3	(S_a,S_a,S_C,S_C)-**L2**	500	20	1	92	66	2	32	rac
4	(S_a,S_a,R_C,R_C)-**L2**	500	20	1	>99	34	11	54	74(*S*)
5	(S_a,S_a,R_C,R_C)-**L2**	200	−20	2.5	>99	85	2	13	88(*S*)
6	(S_a,S_a,R_C,R_C)-**L2**	200	−30	2.5	96	99	—	1	91(*S*)

[a] Selectivity refers to products of styrene.[19]

considerable amounts of products from the consecutive isomerisation and oligomerisation reactions (entry 4). More importantly, product **3** was obtained with an enantioselectivity of 74% (*S*) ee. Lowering the reaction temperature to −20 °C, both selectivity and ee could be improved to 85% and 88%, respectively (entry 5). Finally, carrying out the hydrovinylation at −30 °C (entry 6), the consecutive reactions could be suppressed and 3-phenyl-but-1-ene was obtained with almost perfect selectivity[19] and an ee of 91% (*S*). This enantioselectivity value is at the same level as that achieved with benchmark catalytic systems under comparable conditions, while the catalyst activity (TOF_{av} of 80 h^{-1}) is circa one order of magnitude lower. Noticeably, the new catalytic system allowed high selectivity towards **3** also at very high styrene conversion (entry 6) indicating that it is less prone to promote the isomerisation and other consecutive reactions in comparison to BINOL-based phosphoramidites.[18a]

Conclusions

By careful choice of the conditions, the reaction of 1,1-dichloro-*N*,*N*-bis(1-phenylethyl)phosphinamine **1** with (S_a)-*N*-Ph-NOBIN can be steered toward the selective formation of P-stereogenic phosphorodiamidite **L1** with a chelating NOBIN moiety or phosphoramidite **L2** with three non-bridged substituents (Fig. 2).

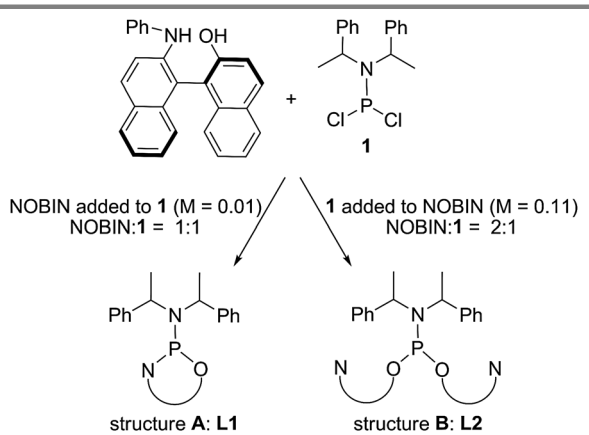


Fig. 2 Synthesis of phosphoramidites *vs.* phosphorodiamidite ligands.

All chiral phosphoramidites successfully applied in catalysis today are based on a diol and a monoamine,[3,20] and the presence of a cyclic unit is believed to ensure high stability as a necessity to impart a definite stereo-arrangement to the resulting ligand.[3] In this respect, (S_a,S_a,R_C,R_C)-**L2**, composed of two (amino)alcohol moieties and a monoamine, is unique and is the first phosphoramidite of this type leading to a highly enantioselective catalytic transformation. The striking difference in the enantioselectivity obtained with two diastereomers of **L2** shows once again the importance of cooperative effects between the various chiral elements within the ligand structure.[21] An intervention of the free NH functionalities during the catalytic cycle cannot be excluded at this stage.

Experimental section

General remarks

All reactions and manipulations were performed using standard Schlenk techniques or in a glovebox under an argon atmosphere. ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded on a Bruker AV 600 (600, 150 and 243 MHz, respectively). Chemical shifts were referenced to residual solvent peaks (^{1}H-NMR, ^{13}C-NMR) or H_3PO_4 85% as external standard (^{31}P-NMR). Mass spectra were recorded on a Finnigan MAT 95 (HRMS-ESI). Optical rotations were measured on a Jasco P-1020 polarimeter. The concentrations used for measuring specific rotations are given as g per 100 mL. CH_2Cl_2 and *n*-pentane were dried over alumina and molecular sieves with a solvent purification system from Innovative Technology. NEt_3 was freshly distilled from KOH. $CDCl_3$ was degassed through freeze–pump–thaw cycles and stored above molecular sieves. The following substances have been synthesised according to literature procedures: (S_a)-NOBIN,[22] (S_a)-*N*-Ph-NOBIN,[23] (S_C,S_C)-**1** and (R_C,R_C)-**1**,[24] NaBArF,[25] [Ni(allyl)Br]$_2$.[26] Ethylene (purity 2.5) was purchased from Westfalen AG. Silica gel (SiO_2 60, 0.04–0.063 mm, 230–400 mesh) was purchased from Roth. All other chemicals were purchased from Sigma-Aldrich or Alfa Aesar and used as received.

Ligand synthesis

(11b*S*)-5-Phenyl-*N*,*N*-bis((*S*)-1-phenylethyl)dinaphtho[2,1-*d*:1′,2′-*f*]-[1,3,2]oxazaphosphepin-4(5*H*)-amine, (S_a,S_C,S_C,R_P)-L1. To a solution of (S_C,S_C)-**1** (229.7 mg, 0.704 mmol) in CH_2Cl_2 (70 mL) at 0 °C was added NEt_3 (10 eq., 0.98 mL, 7.04 mmol) *via* a syringe and then dropwise a solution of (S_a)-*N*-Ph-NOBIN (254.5 mg, 0.704 mmol) in the same solvent (30 mL). The reaction

mixture was stirred at rt for 16 h and then the volatiles were removed under reduced pressure. The resulting yellowish solid was purified *via* flash column chromatography (SiO_2, CH_2Cl_2 : *n*-pentane = 2 : 5; (S_a,S_C,S_C,R_P)-**L1**: Rf = 0.79, (S_a,S_a,S_C,S_C)-**L2**: Rf = 0.61). Yield: (S_a,S_C,S_C,R_P)-**L1** = 194 mg (45%); (S_a,S_a,S_C,S_C)-**L2** = 83 mg (12%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.04 (d, 1H, J = 8.8 Hz, Ar), 7.97 (d, 1H, J = 8.2 Hz, Ar), 7.90 (d, 1H, J = 7.9 Hz, Ar), 7.81 (d, 1H, J = 8.8 Hz, Ar), 7.68 (d, 1H, J = 8.8 Hz, Ar), 7.54 (d, 1H, J = 8.8 Hz, Ar), 7.51 (m, 1H, Ar), 7.48–7.42 (m, 3H, Ar), 7.39–7.31 (m, 8H, Ar), 7.28–7.22 (m, 4H, Ar), 6.85–6.76 (m, 3H, Ar), 6.22 (d, 2H, J = 7.9 Hz, Ar), 4.54 (m, 2H, C*H*CH_3), 1.84 (d, 6H, J = 7.0 Hz, CH_3) ppm. ^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ = 150.60 (C_q), 148.20 (d, J = 26.2 Hz, C_q), 143.10 (d, J = 1.4 Hz, 2C_q), 141.84 (d, J = 5.4 Hz, C_q), 133.12 (d, J = 2.4 Hz, C_q), 132.83 (C_q), 131.83 (C_q), 131.32 (C_q), 130.37 (CH), 129.88 (C_q), 129.59 (CH), 128.92 (2CH), 128.90 (2CH), 128.60 (d, J = 1.4 Hz, 2CH), 128.51 (CH), 128.11 (2CH), 128.05 (CH), 128.03 (4CH), 127.14 (2CH), 126.55 (CH), 126.21 (CH), 126.06 (CH), 125.84 (d, J = 5.5 Hz, C_q), 125.45 (CH), 124.59 (CH), 122.52 (d, J = 2.3 Hz, CH), 121.42 (CH), 121.07 (d, J = 12.7 Hz, 2CH), 54.21 (*C*HCH_3), 54.14 (*C*HCH_3), 21.85 (2CH*C*H_3) ppm. ^{31}P{^{1}H}-NMR (243 MHz, $CDCl_3$): δ = 142.72. HRMS (ESI): m/z = calcd for $C_{68}H_{54}N_3O_2P$: 614.24815; found: 614.24627; $[\alpha]_D^{20}$ = −258° (c = 0.1, CH_2Cl_2).

(11b*S*)-5-Phenyl-*N*,*N*-bis((*R*)-1-phenylethyl)dinaphtho[2,1-*d*:1′,2′-*f*]-[1,3,2]oxazaphosphepin-4(5*H*)-amine (S_a,R_C,R_C,R_P)-L1. The same procedure as above. (R_C,R_C)-**1** was used instead of (S_C,S_C)-**1**. Purification *via* flash column chromatography (SiO_2, CH_2Cl_2 : *n*-pentane = 2 : 5; (S_a,R_C,R_C,R_P)-**L1**: Rf = 0.75, (S_a,S_a,R_C,R_C)-**L2**: Rf = 0.64). Yield: (S_a,R_C,R_C,R_P)-**L1** = 151 mg (35%); (S_a,S_a,R_C,R_C)-**L2** = 90 mg (13%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.96–7.93 (m, 3H, Ar), 7.92 (d, 1H, J = 8.1 Hz, Ar), 7.62 (d, 1H, J = 8.8 Hz, Ar), 7.51–7.44 (m, 4H, Ar), 7.35–7.28 (m, 3H, Ar), 7.20–7.12 (m, 12H, Ar), 7.08 (d, 2H, J = 8.1 Hz, Ar), 6.94 (7, 1H, J = 7.3 Hz, Ar), 4.60 (m, 2H, C*H*CH_3), 1.93 (d, 6H, J = 7.0 Hz, CH_3) ppm. ^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ = 149.89 (C_q), 148.44 (d, J = 26.0 Hz, C_q), 142.73 (b, 2C_q), 141.62 (d, J = 4.2 Hz, C_q), 132.93 (d, J = 2.2 Hz, C_q), 132.74 (C_q), 131.85 (C_q), 131.22 (d, J = 1.2 Hz, C_q), 130.32 (C_q), 130.15 (CH), 129.36 (CH), 128.76 (d, J = 1.3 Hz, 2CH), 128.47 (CH), 128.24 (4CH), 128.05 (CH), 127.97 (CH), 127.76 (CH), 127.67 (4CH), 126.58 (2CH), 126.37 (CH), 126.08 (CH), 126.03 (CH), 125.77 (d, J = 5.5 Hz, C_q), 125.50 (CH), 124.45 (CH), 122.20 (d, J = 2.3 Hz, CH), 121.78 (CH), 121.18 (d, J = 13.2 Hz, 2CH), 54.12 (*C*HCH_3), 54.05 (*C*HCH_3), 22.15 (2CH*C*H_3) ppm. ^{31}P{^{1}H}-NMR (243 MHz, $CDCl_3$): δ = 135.00. HRMS (ESI): m/z = calcd for $C_{68}H_{54}N_3O_2P$: 614.24815; found: 614.24792; $[\alpha]_D^{20}$ = 579° (c = 0.1, CH_2Cl_2).

(1′*S*,1″*S*)-2′,2″-((bis((*S*)-1-Phenylethyl)amino)phosphinediyl)-bis(phenylazanediyl)di-1,1′-bibenzobenzen-2-ol, (S_a,S_a,S_C,S_C)-L2. To a solution of (S_a)-*N*-Ph-NOBIN (2 eq., 211.9 mg, 0.584 mmol) in CH_2Cl_2 (5 mL) at 0 °C was added NEt_3 (20 eq., 0.81 mL, 5.84 mmol) *via* a syringe and then dropwise a solution of (S_C,S_C)-**1** (1 eq., 95.3 mg, 0.292 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at rt for 5 h and then the volatiles were removed under reduced pressure. The resulting yellowish solid was purified *via* flash column chromatography (SiO_2 60, CH_2Cl_2 : *n*-pentane = 2 : 5; (S_a,S_a,S_C,S_C)-**L2**: Rf = 0.61). Yield = 198 mg (69%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.99 (d, 1H, J = 8.0 Hz, Ar), 7.93 (d, 1H, J = 9.1 Hz, Ar), 7.90 (d, 1H, J = 8.9 Hz, Ar), 7.89 (d, 1H, J = 7.9 Hz, Ar), 7.86 (d, 1H, J = 8.3 Hz, Ar), 7.81 (d, 1H, J = 9.0 Hz, Ar), 7.71 (d, 1H, J = 9.0 Hz, Ar), 7.69 (d, 1H, J = 8.3 Hz, Ar), 7.49 (m, 1H, Ar), 7.44 (m, 1H, Ar), 7.38–7.29 (m, 7H, Ar), 7.27–7.23 (m, 5H, Ar), 7.22–7.17 (m, 2H, Ar), 7.10–7.05 (m, 7H, Ar), 7.03 (d, 1H, J = 8.5 Hz, Ar), 6.98 (t, 1H, J = 7.4 Hz, Ar), 6.92 (t, 2H, J = 7.9 Hz, Ar), 6.72 (t, 1H, J = 7.4 Hz, Ar), 6.67 (d, 2H, J = 7.7 Hz, Ar), 6.65–6.59 (m, 4H, Ar), 6.48 (d, 1H, J = 8.9 Hz, Ar), 6.17 (d, 1H, J = 9.0 Hz, Ar), 5.61 (s, 1H, OH), 5.55 (s, 1H, OH), 4.31 (s br, 2H, C*H*CH_3), 0.87 (d, 6H, J = 8.0 Hz, CH_3) ppm. ^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ = 150.59 (d, J = 6.3 Hz, C_q), 150.43 (d, J = 7.6 Hz, C_q), 143.07 (C_q), 142.91 (C_q), 142.63 (2C_q), 139.83 (C_q), 139.61 (C_q), 134.95 (C_q), 134.82 (C_q), 134.24 (C_q), 133.61 (C_q), 130.53 (C_q), 130.08 (C_q), 129.72 (C_q), 129.54 (C_q), 129.46 (CH), 129.39 (CH), 129.32 (2CH), 128.94 (2CH), 128.90 (CH), 128.75 (CH), 128.35 (4CH), 128.29 (CH), 128.14 (2CH), 127.95 (CH), 127.77 (4CH), 126.84 (CH), 126.81 (2CH), 126.44 (2CH), 126.43 (CH), 125.81 (2CH), 125.65 (CH), 125.42 (CH), 124.48 (2CH), 123.43 (CH), 123.17 (CH), 121.67 (CH), 121.60 (d, J = 2.9 Hz, C_q), 121.02 (d, J = 2.6 Hz, C_q), 120.95 (CH), 120.56 (d, J = 11.6 Hz, CH), 119.91 (d, J = 17.5 Hz, CH), 119.54 (2CH), 119.32 (CH), 118.99 (C_q), 118.32 (2CH), 118.30 (C_q), 117.90 (CH), 51.81 (*C*HCH_3), 51.74 (*C*HCH_3), 20.67 (2CH*C*H_3) ppm. ^{31}P{^{1}H}-NMR (243 MHz, $CDCl_3$): δ = 141.17. HRMS (ESI): m/z = calcd for $C_{68}H_{54}N_3O_2P$: 975.39482; found: 975.39520; $[\alpha]_D^{20}$ = 173° (c = 0.1, CH_2Cl_2).

(1′*S*,1″*S*)-2′,2″-((bis((*R*)-1-Phenylethyl)amino)phosphinediyl)-bis(phenylazanediyl)di-1,1′-bibenzobenzen-2-ol, (S_a,S_a,R_C,R_C)-L2. The same procedure as above. (R_C,R_C)-**1** was used instead of (S_C,S_C)-**1**. Purification *via* flash column chromatography (SiO_2, CH_2Cl_2 : *n*-pentane = 2:1); yield: = 199 mg (70%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.96 (d, 1H, J = 9.0 Hz, Ar), 7.93–7.89 (m, 3H, Ar), 7.85 (d, 1H, J = 8.0 Hz, Ar), 7.80 (d, 1H, J = 8.2 Hz, Ar), 7.69 (d, 1H, J = 9.0 Hz, Ar), 7.64 (d, 1H, J = 9.0 Hz, Ar), 7.62 (d, 1H, J = 8.9 Hz, Ar), 7.48 (m, 1H, Ar), 7.48–7.42 (m, 1H, Ar), 7.39–7.35 (m, 2H, Ar), 7.32–7.25 (m, 5H, Ar), 7.25–7.18 (m, 3H, Ar), 7.17–7.07 (m, 6H, Ar), 7.02–6.97 (m, 3H, Ar), 6.91–6.87 (m, 2H, Ar), 6.84–6.78 (m, 6H, Ar), 6.67 (d, 2H, J = 7.6 Hz, Ar), 6.64 (d, 1H, J = 8.9 Hz, Ar), 6.45 (d, 1H, J = 7.6 Hz, Ar), 6.28 (d, 1H, J = 9.0 Hz, Ar), 5.39 (s, 1H, NH), 5.18 (s, 1H, NH), 4.33 (m, 2H, C*H*CH_3), 0.95 (d, 6H, J = 7.2 Hz, CH_3) ppm. ^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ = 150.84 (d, J = 8.6 Hz, C_q), 150.30 (d, J = 1.8 Hz, C_q), 142.98 (2C_q), 142.57 (C_q), 142.24 (C_q), 140.86 (C_q), 139.78 (C_q), 134.35 (C_q), 134.18 (C_q), 133.47 (C_q), 133.42 (C_q), 130.97 (C_q), 130.25 (CH), 129.97 (C_q), 129.47 (C_q), 129.38 (CH), 129.28 (C_q), 129.05 (2CH), 129.01 (CH), 128.96 (2CH), 128.82 (CH), 128.41 (4CH), 128.40 (CH), 128.08 (CH), 127.99 (CH), 127.87 (5CH), 126.96 (CH), 126.85 (CH), 126.81 (2CH), 126.53 (CH), 126.28 (CH), 125.37 (CH), 125.35 (CH), 125.10 (CH), 125.08 (CH), 124.96 (CH), 124.35 (CH), 123.14 (CH), 123.13 (CH), 122.83 (d, J = 3.5 Hz, C_q), 122.74 (d, J = 5.7 Hz, CH), 121.84 (2CH), 120.32 (2CH), 120.27

(d, J = 2.0 Hz, C_q), 120.07 (2CH), 119.50 (d, J = 20.5 Hz, CH), 117.79 (C_q), 117.64 (CH), 117.42 (CH), 117.41 (C_q), 52.25 ($CHCH_3$), 52.17 ($CHCH_3$), 20.84 ($2CHCH_3$) ppm. $^{31}P\{^1H\}$-NMR (243 MHz, $CDCl_3$): δ = 141.37. HRMS (ESI): m/z = calcd for $C_{68}H_{54}N_3O_2P$: 975.39482; found: 975.39497 $[\alpha]_D^{20} = -110^\circ$ (c = 0.1, CH_2Cl_2).

Hydrovinylation procedure

To a solution of $[Ni(allyl)Br]_2$ in CH_2Cl_2 (1 mL, 5.4×10^{-3} M) at 0 °C was added a solution of the ligand (1 mL, 0.011 M) in the same solvent. After 15 min, NaBArF (10.6 mg, 0.012 mmol) was added as a solid and the mixture stirred at rt for 30 minutes. The mixture was then cooled down to the desired temperature (see Table 1) and the inert gas exchanged for ethylene by bubbling it through the solution for 5 s. Then, the appropriate amount of styrene (see Table 1) was added and the mixture vigorously stirred and kept under an ethylene atmosphere at ambient pressure during the reaction time. Saturated aqueous NH_4Cl (4 mL) and the GC-standard ethylbenzene (equimolar amount to styrene) were added. The organic phase was separated, dried over Na_2SO_4, filtered through a short pad of silica and analysed by GC.

Acknowledgements

We thank H. Eschmann and J. Wurlitzer for GC measurements, Ms B. Pütz for the measurement of MS data, and Dr. M. Hölscher for DFT calculations. The research leading to these results has received funding from the European Community's Seventh Framework Program under grant agreement no. 246461.

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