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Synthesis of Chiral, Monodentate Aminophosphane and Phosphoramidite Ligands Derived from Amino Acid Esters: Application in Rh-Catalysed Asymmetric Olefin Hydrogenation Reactions

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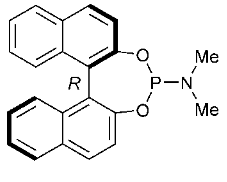
Six chiral monodentate ligands combining a 1,3-dioxa-2-phosphacycloheptadinaphthyl moiety [(*R*)- or (*S*)-binoP] either with a phenylalanine- or with an alanine-derived fragment were synthesised. The new phosphoramidites are all relatively air stable. Related compounds in which the binoP moiety was replaced by a diphenylphosphanyl group were also prepared for comparison. The X-ray structures of two phosphoramidite complexes, *cis*-$PtCl_2[(R)\text{-binoP–NMeR}]_2$ [**5**, R = (*R*)-$CH(CH_2Ph)(CO_2Me)$; **6**, R = (*S*)-$CH(CH_2Ph)(CO_2Me)$], were determined by single X-ray analysis. In the solid state, both structures are nearly C_2 symmetric, and the nitrogen atoms lies out of the coordination plane. Owing to the particular orientation of the benzyl groups in **6**, the environment of the coordination sites occupied in this complex by the chlorine atoms is sterically more crowded than in **5**. In the hydrogenation of 2-(acetylamino)-3-(aryl)propenoic methyl esters (aryl = 4-X-C_6H_4, X = H, F, Cl; aryl = 3,4-Cl_2–C_6H_3), the alanine-derived phosphoramidites turned out to be ca. twice as active as the corresponding phenylalanine analogues. The highest *ee*'s were observed with the phenylalanine derivatives, for example 92 % in the hydrogenation of 2-(acetylamino)-3-(phenyl)propenoic methyl ester, by using (*R*)-binoP–NMe-(*R*)-$CH(CH_2Ph)(CO_2Me)$.

Introduction

In the last three decades natural amino acids and their derivatives have been often used as chiral backbones in the synthesis of optically active diphosphanes suitable for the enantioselective rhodium(I)-, ruthenium(II)- or iridium(I)-catalysed hydrogenation of prochiral unsaturated substrates.[1–4] For example, amino alcohols such as valinol, leucinol and prolinol gave access to a variety of mixed bidentate ligands, in particular aminophosphonite–phosphites,[5] aminophosphonite–phosphinites or aminophosphane–phosphinites[6–18] many of which turned out to give high enantiomeric excesses (*ee*'s) in enantioselective catalysis.

Recently, Feringa and Reetz found that monodentate, chiral phosphoramidite ligands, such as **A**, in which the phosphorus atom is part of a rigid, seven-membered ring involving a 1,1′-binaphthyl unit may lead to high conversions and enantiomeric excesses in metal-catalysed hydrogenations.[19–27] In their seminal works, they independently demonstrated that these readily accessible monodentate ligands give equivalent if not better results than conventional P^{III} bidentate ligands.[28] The way these catalysts operate is still a matter of debate and a better understanding of their performance requires not only the synthesis and study of new variants of such ligands, but also solid-state studies that may establish particular structural features of their metal complexes.



A

The present work describes the synthesis and structural characterisation of chiral *monodentate* ligands associating, for the first time, a phosphoramidite coordinating unit with the bulky and easily accessible *phenylalanine* backbone (Scheme 1). We also prepared ligands in which the latter was replaced by the less sterically demanding *alanine* fragment as well as some diphenylphosphanyl analogues of these phosphoramidites. A comparative study of their catalytic properties for the asymmetric rhodium-catalysed hydrogenation of α-*N*-acetaminoacrylic esters was carried out to assess the importance of the amino acid backbone on both catalyst selectivity and activity. In the following, the

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indexes “Bn”, “Me” and “bin” refer to molecules containing –NMeCH(*CH_2Ph*)(CO_2Me), –NMeCH(*Me*)(CO_2Me) and *binaphthyl* groups, respectively. To date, monophosphoramidites that bear oxygen-containing pending groups have only been mentioned in two publications, one dealing with an ester[25] and the other with an ether[29] substituent.

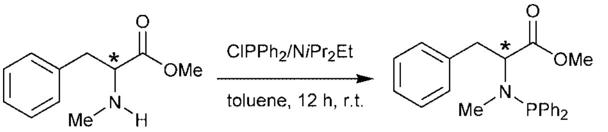
(*R* or *S*)-*N*-methylphenylalanine methyl ester (*S*)-*N*-methylalanine methyl ester

Scheme 1. Phenylalanine and alanine derivatives used in this study as building blocks for the construction of chiral phosphanes.

Results and Discussion

Ligand Synthesis and Characterisation

We began this study by preparing aminophosphanes (S_{Bn})-**2a** and (R_{Bn})-**2b** (Scheme 2). These were obtained in ca. 85% yield by treating chlorodiphenylphosphane with (*S*)- and (*R*)-*N*-methylphenylalanine methyl ester, respectively, in the presence of 1 equiv. of diisopropylethylamine. We noted that the replacement of the latter amine by a less sterically hindered one, notably triethylamine, produced significant amounts of byproducts. The two aminophosphanes are relatively air stable and can be stored in air without particular care for months. Both products are characterised by a single peak at δ = 67.9 ppm in their $^{31}P\{^1H\}$ NMR spectra, a value that lies in the range found for similar ligands.[30]

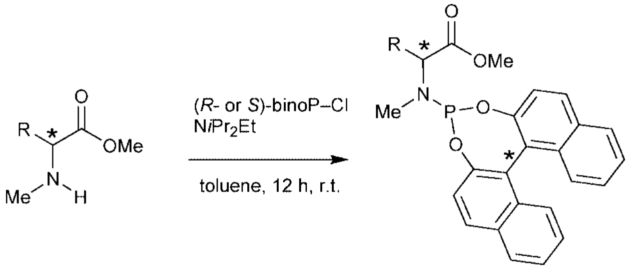


(S_{Bn})-**1a**
(R_{Bn})-**1b**

(S_{Bn})-**2a**
(R_{Bn})-**2b**

Scheme 2. Synthesis of aminophosphanes **2a** and **2b**.

To increase the chiral load of the molecules, we embarked on the synthesis of phosphoramidite ligands incorporating a 1,1′-binaphthyl unit in addition to a phenylalanine-derived fragment. Thus, the four stereoisomers (S_{Bn},S_{bin})-**3a**, (R_{Bn},R_{bin})-**3b**, (R_{Bn},S_{bin})-**3c** and (S_{Bn},R_{bin})-**3d**, all containing a –NMeCH(CH_2Ph)(CO_2Me) moiety, were synthesised (Scheme 3) from [(*R* or *S*)-(1,1′-binaphthalene-2,2′-diyl)] chlorophosphite (binoPCl[31]) and the appropriate amino acid ester according to the method described above. The two diastereoisomers (S_{Me},R_{bin})-**4a** and (S_{Me},S_{bin})-**4b**, containing the (*S*)-alanine-derived –NMeCH(Me)(CO_2Me) fragment, were obtained by treatment of [(S_{Me})-**1c**]HCl with 2 equiv. of diisopropylethylamine and 1 equiv. of the corresponding chlorophosphite (Scheme 3). As expected for phosphoramidite ligands, all six compounds can be handled in air without noticeable oxidation, but they undergo P–N cleavage in the presence of water. The NMR spectra of the diastereoisomeric pairs of enantiomers (S_{Bn},S_{bin})-**3a**/(R_{Bn},R_{bin})-**3b** and (R_{Bn},S_{bin})-**3c**/(S_{Bn},R_{bin})-**3d**, in particular the $^{31}P\{^1H\}$ NMR spectra, which consist of single peaks at δ = 149.0 and 148.6 ppm,[32] are nearly identical. Similar small spectroscopic differences are observed between (S_{Me},R_{bin})-**4a** and (S_{Me},S_{bin})-**4b** [$\delta(^{31}P)$ = 148.5 and 148.2 ppm, respectively]. We note that whereas the H*C*(CO) carbon atom of (S_{Bn})-**2a** is low-field shifted with respect to that of the parent amine, MeNHCHR(CO_2Me), in the phosphoramidite (S_{Bn},S_{bin})-**3a** the corresponding carbon atom has undergone a high-field shift (Figure 1).



(S_{Bn})-**1a**; R = benzyl
(R_{Bn})-**1b**; R = benzyl
[(S_{Me})-**1c**]HCl; R = methyl

(S_{Bn},S_{bin})-**3a**; R = benzyl
(R_{Bn},R_{bin})-**3b**; R = benzyl
(R_{Bn},S_{bin})-**3c**; R = benzyl
(S_{Bn},R_{bin})-**3d**; R = benzyl
(S_{Me},R_{bin})-**4a**; R = methyl
(S_{Me},S_{bin})-**4b**; R = methyl

Scheme 3. Synthesis of the phosphoramidites **3** and **4**.

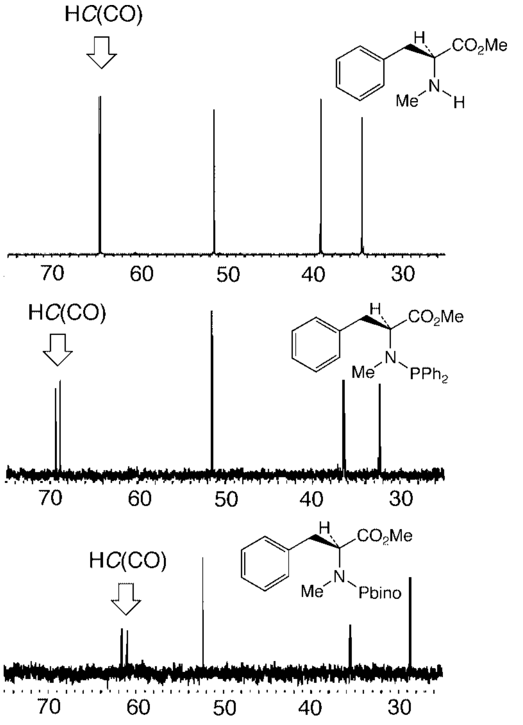


Figure 1. Part of the ^{13}C NMR spectra ($CDCl_3$) of S_{Bn}-**1a**, S_{Bn}-**2a** and (S_{Bn},S_{bin})-**3a**. The arrows show the signals of the H*C*(CO_2Me) carbon atoms.

To verify that the phosphoramidites described above are suitable to form square-planar complexes having two *cis* disposed phosphanes, which is the typical stereochemistry in most hydrogenation catalysts, we investigated the coordination properties of (R_{Bn},R_{bin})-**3b** and (S_{Bn},R_{bin})-**3d** towards platinum(II). The reaction of these ligands with [$PtCl_2$(cod)] (cod = 1,5-cyclooctadiene) or [$PtCl_2$(dcpd)] (dcpd = dicyclopentadiene) afforded complexes **5** and **6**, respectively (Scheme 4; see Experimental Section). The stereochemistry of the complexes was inferred from the corresponding ^{31}P NMR spectra, which both consist of a singlet flanked by two Pt satellites, with a $J_{P,Pt}$ coupling constant (5579 Hz for both complexes) in accord with the value reported by Hope et al. for another platinum phosphoramidite complex, namely *cis*-[$PtCl_2$(monophos)$_2$] (where monophos stands for ligand **A**).[33,34]

The stereochemistry of the complexes was further confirmed by single-crystal X-ray diffraction studies (Figure 2). The unit cell of **5** contains two inequivalent molecules (**5a** and **5b**), which structurally differ only a little, whereas that of **6** contains a single type of molecule. In both structures the molecules are nearly C_2 symmetric, and the nitrogen atoms are located out of the coordination plane [N to plane distances in **5a**: +1.31(1) and –1.31(1) Å; in **5b**: +1.32(1) and –1.31(1) Å; in **6**: +1.38(1) and –1.39(1) Å]. In all these molecules, the metal centre lies in an almost planar coordination environment, but the P–Pt–P angles are considerably larger than 90° [97.5(1)° and 97.6(1)° in **5**; 100.6(1)° in **6**], thus reflecting the steric bulk of the phosphane moieties. Similar deviations from an ideal square-planar coordination geometry were observed in the few structurally characterised binaphthyl-containing [MX_2(phosphoramidite)$_2$] complexes.[20,33] In both structures the nitrogen atoms are in a quasiplanar environment, and hence show that the electron-donating effect of the nitrogen atom onto the phosphorus atom is operating. The bond lengths about the metal centres are normal (see caption of Figure 2).

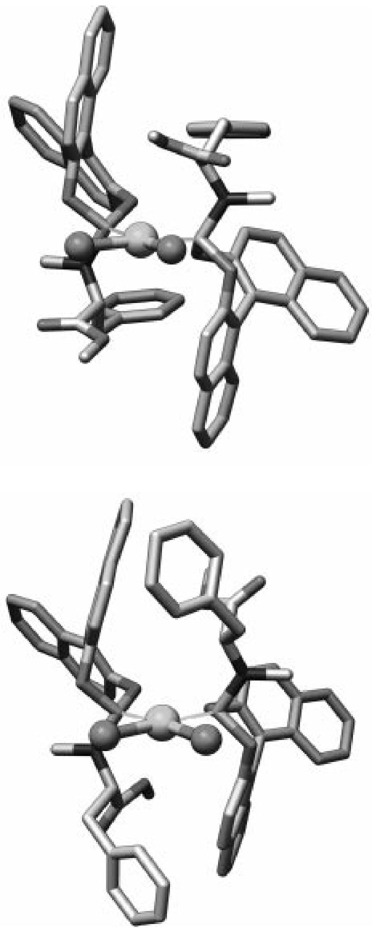
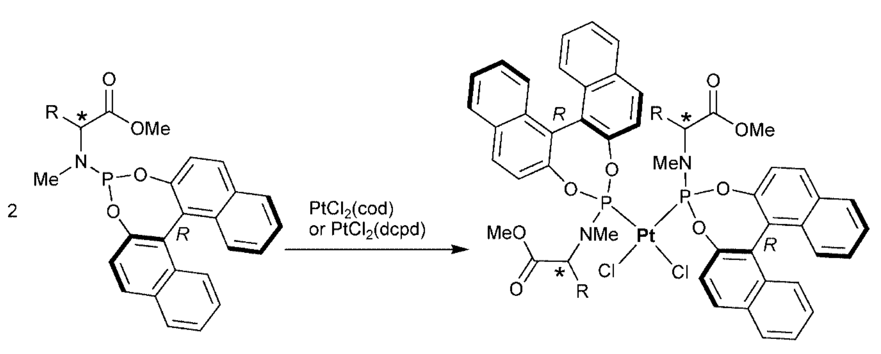


Figure 2. X-ray structures of compound **5a** (top) and compound **6** (bottom) showing the steric protection of the chloride atoms. Important bond lengths [Å]: **5a**: P(1)–Pt 2.207(3), P(2)–Pt 2.200(3), Pt–Cl(1) 2.336(3), Pt–Cl(2) 2.336(3), P(1)–N(1) 1.62(1), P(2)–N(2) 1.63(1); **6**: P(1)–Pt 2.222(2), P(2)–Pt 2.213(3), Pt–Cl(1) 2.349(3), Pt–Cl(2) 2.339(3), P(1)–N(1) 1.59(1), P(2)–N(2) 1.62(1). Dihedral angles [°] between the linked naphthyl units, in **5a**: 58.6 and 57.8; in **6**: 60.5 and 56.3.

If the coordination plane is taken as a reference plane, the halide atoms of complex **5** may be viewed both as apically protected by a –CO_2Me moiety and a naphthyl group; these fragments belong to the same P^{III} ligand and are located on either side of the plane. In complex **6**, the steric protection about each halide is markedly increased on one side of the plane, because here the benzyl groups occupy domains previously occupied by the smaller ester moieties.



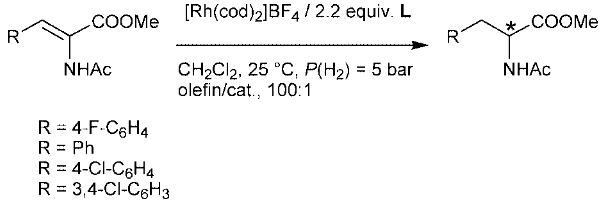
(R_{Bn},R_{bin})-**3b**
(S_{Bn},R_{bin})-**3d**

5
6

Scheme 4. Synthesis of platinum complexes **5** and **6**.

Catalytic Studies

For the catalytic study, we focussed our attention on the reduction of 2-(acetylamino)-3-(4-fluorophenyl)propenoic methyl ester. A literature search revealed that this fluorinated amino acid has been relatively little studied. Some related compounds were also studied for comparison (Scheme 5).



Scheme 5. Hydrogenation of 2-(acetylamino)-3-arylpropenoic methyl esters.

All catalytic runs (Table 1) were performed with in-situ-generated catalysts under 5 bar pressure by using an olefin/rhodium ratio of 100:1. It turned out that operating at r.t. afforded slightly higher yields than at 0 °C (Table 1, Entries 4 and 21). Further, among the solvents tested (thf, MeOH, AcOEt, CH_2Cl_2), dichloromethane gave the highest enantioselectivity (Table 1, Entries 1–3 and 21). In the following, we will therefore only discuss those runs performed at r.t. and in dichloromethane. As expected, we found that enantiomeric complexes (e.g. **3a** and **3b**) gave enantiomeric hydrogenation compounds; the *ee*'s were the same within experimental error.

As a general trend, and consistent with literature reports, the hydrogenation rates observed with the phosphoramidites were ca. 2–4 times better than those obtained with the aminophosphanes. We also found that aminophosphanes **2a** and **2b** resulted in very weak *ee*'s in the hydrogenation of 2-(acetylamino)-3-(phenyl)propenoic methyl ester and 2-(acetylamino)-3-(4-fluorophenyl)propenoic methyl ester (Table 1, Entries 5, 6, 19 and 20). This may be attributed to the fact that in the corresponding aminophosphane complexes the stereogenic centres are relatively far from the metal centre. We further observed that higher enantioselectivities were found for L/Rh ratios ≥ 2 (Table 1, compare Entry 8 with Entries 9–11, and compare Entry 12 with Entries 13–15) than for lower ratios. It is likely that L/Rh ratios below 2 result in part in the formation of [RhL(cod)]-BF_4 complexes in which the phosphoramidite behaves as a chelating ligand (possibly as a P,O rather than a P,N che-

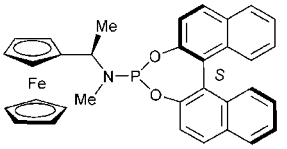
Table 1. Enantioselective hydrogenation of α-dehydroamino esters by a Rh–monodentate phosphoramidite catalyst.[a]

Entry	R	Ligand	Solvent	Time [h]	Conversion[b] [%]	*ee*[c] [%]	Configuration
1	(4-F)-Ph	**3a**	thf	16	100	47	*R*
2	(4-F)-Ph	**3a**	MeOH	16	100	37	*R*
3	(4-F)-Ph	**3a**	EtOAc	16	100	35	*R*
4[d]	(4-F)-Ph	**3a**	CH_2Cl_2	16	75	86	*R*
5	Ph	**2a**	CH_2Cl_2	24	93	2	*R*
6	Ph	**2b**	CH_2Cl_2	24	90	2	*S*
7	Ph	**3a**	CH_2Cl_2	24	100	90	*R*
8	Ph	**3b**	CH_2Cl_2	24	100	92	*S*
9[e]	Ph	**3b**	CH_2Cl_2	24	100	69	*S*
10[f]	Ph	**3b**	CH_2Cl_2	24	100	83	*S*
11[g]	Ph	**3b**	CH_2Cl_2	24	100	90	*S*
12	Ph	**3c**	CH_2Cl_2	24	93	87	*R*
13[e]	Ph	**3c**	CH_2Cl_2	24	86	79	*R*
14[f]	Ph	**3c**	CH_2Cl_2	24	85	81	*R*
15[g]	Ph	**3c**	CH_2Cl_2	24	86	85	*R*
16	Ph	**3d**	CH_2Cl_2	24	93	90	*S*
17	Ph	**4a**	CH_2Cl_2	18	100	81	*S*
18	Ph	**4b**	CH_2Cl_2	18	100	78	*R*
19	(4-F)-Ph	**2a**	CH_2Cl_2	65	94	8	*R*
20	(4-F)-Ph	**2b**	CH_2Cl_2	65	93	7	*S*
21	(4-F)-Ph	**3a**	CH_2Cl_2	24	90	85	*R*
22	(4-F)-Ph	**3b**	CH_2Cl_2	24	94	88	*S*
23	(4-F)-Ph	**3c**	CH_2Cl_2	24	12	67	*R*
24	(4-F)-Ph	**3d**	CH_2Cl_2	24	14	68	*S*
25	(4-F)-Ph	**4a**	CH_2Cl_2	18	100	78	*S*
26	(4-F)-Ph	**4b**	CH_2Cl_2	18	100	76	*R*
27	(3,4-Cl)-Ph	**3a**	CH_2Cl_2	24	98	85	*R*
28	(3,4-Cl)-Ph	**3b**	CH_2Cl_2	24	96	84	*S*
29	(4-Cl)-Ph	**3a**	CH_2Cl_2	24	98	89	*R*
30	(4-Cl)-Ph	**3b**	CH_2Cl_2	24	99	92	*S*
31	Ph	**3b+3d**	CH_2Cl_2	19	14	89	*S*
32	Ph	**3d+4a**	CH_2Cl_2	19	32	92	*S*

[a] General conditions: $P(H_2)$ = 5 bar; T = r.t.; substrate/Rh/ligand, 100:1:2.2. [b] Conversions were determined by means of ^1H NMR spectroscopic analysis. [c] Enantioselectivities were determined by chiral GC analysis by using a CHROMPAK chiral fused silica 25 m × 0.25 mm i.d. and/or specific rotation. Coating Chirasil-L-Val column. [d] Reaction carried out at 0 °C. [e] Substrate/Rh/ligand, 100:1:1. [f] Substrate/Rh/ligand, 100:1/1.5. [g] Substrate/Rh/ligand, 100:1:2.5.

late), which in turn give lower *ee*'s than the corresponding [Rh(phosphoramidite)$_2$(cod)]BF$_4$ complexes. Note that complexes of the latter type are generally formed when 2 equiv. of a monophosphoramidite are reacted with [Rh(cod)$_2$]BF$_4$.[20]

The highest *ee*'s, 92%, were obtained with phosphoramidite (R_{Bn},R_{bin})-**3b** (Table 1, Entries 8 and 30) in the hydrogenation of 2-(acetylamino)-3-(phenyl)propenoic methyl ester and 2-(acetylamino)-3-(4-chlorophenyl)propenoic methyl ester. The use of the same ligand for the hydrogenation of the fluorinated dehydroaminated ester (Table 1, Entry 22) gave an *ee* of 88%. It must be emphasised here that the performance of this ligand lies slightly below that of the reference ligand **A** [*ee*'s of ca. 95% for 2-(acetylamino)-3-(phenyl)propenoic methyl ester], which in contrast to **3b** contains an achiral amino substituent.[35] Interestingly, the number of binol-derived phosphoramidites in which the amino groups contains a stereogenic centre is limited. A literature survey revealed that, among this class of compounds, only Zheng's phosphoramidite **7**, which is derived from an expensive ferrocenyl–amine, gave better *ee*'s in the hydrogenation of cinammic acid esters than **A**.[36] Significantly lower enantioselectivities than those obtained for **3b** were obtained with proline derivative **8**[25] as well as with phosphoramidite **9**,[35] which contains two stereogenic centres in the amino group. Overall, these findings show that an improvement in the performances of **A** by using variants obtained from cheap, chiral amines remains a difficult task.



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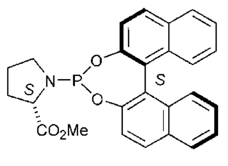

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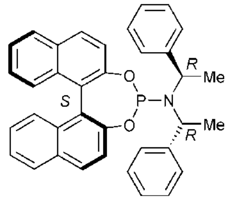

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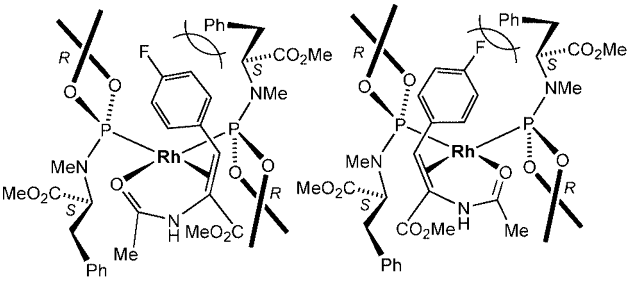
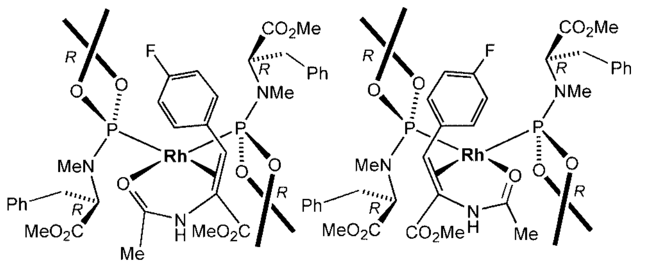
The most surprising result came from diastereomers (R_{Bn},S_{bin})-**3c** and (R_{Bn},R_{bin})-**3b**. Hydrogenation of the fluorinated olefin with (R_{Bn},S_{bin})-**3c** gave only 12% yield after 24 h (Table 1, Entries 23), whereas in the same time the reaction carried out with (R_{Bn},R_{bin})-**3b** was almost complete. Note that such a difference in activity was not observed with these ligands in the reduction of the slightly shorter 2-(acetylamino)-3-(phenyl)propenoic methyl ester (Table 1, Entries 12). Molecular models based on the X-ray structure of complex **6**, which contains ligand (S_{Bn},R_{bin})-**3d**, clearly show that in the hypothetical catalytic intermediates of type α and β (Figure 3), bidentate coordination of the fluorinated olefin results in considerable steric hindrance between the Ar$_{\text{olefin}}$ group and the benzyl groups. In the related **3b**-containing intermediates γ and δ, in which the amino acid ester moiety has a stereochemistry opposite to that of (S_{Bn},R_{bin})-**3d**, coordination of the olefin becomes much more favourable. The olefin–ligand interactions here mainly involve the smaller CO$_2$Me group.



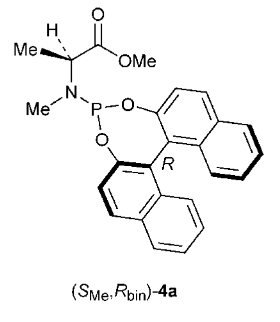
α (containing ligand **3d**) β (containing ligand **3d**)



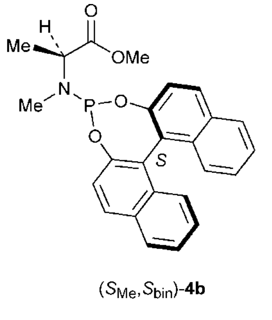
γ (containing ligand **3b**) δ (containing ligand **3b**)

Figure 3. Possible coordination modes involving either complex **5** (α and β) or **6** (γ and δ) and 2-(acetylamino)-3-(4-fluorophenyl)-propenoic methyl ester.

To verify that these interactions have a determining impact on the catalyst activity, we tested ligands (S_{Me},R_{bin})-**4a** and (S_{Me},S_{bin})-**4b**, which contain a methyl group in place of a benzyl group. As anticipated, the hydrogenation reactions carried out with these ligands occurred much faster than those performed with their benzyl analogues (full substrate conversion within 18 h).



(S_{Me},R_{bin})-**4a**



(S_{Me},S_{bin})-**4b**

Furthermore, in the case of (S_{Me},S_{bin})-**4b**, a nonnegligible drop in the asymmetric induction was observed with respect to (S_{Bn},S_{bin})-**3a** in the catalytic reduction of 2-(acetylamino)-3-(phenyl)- and of 2-(acetylamino)-3-(4-fluorophenyl)propenoic methyl ester as well; the *ee*'s decrease by 12 and 9%, respectively (Table 1, Entries 18/7 and 26/21). The same trend was observed on going from (S_{Bn},R_{bin})-**3d** to (S_{Me},R_{bin})-**4a** in the hydrogenation of 2-(acetylamino)-3-(phenyl)propenoic methyl ester; *ee*'s decreased by 9% (Table 1, Entries 17/16). Of course, we have to remain cautious in correlating the observed selectivities and activities, as the rate-determining steps are not known. Note that the hydrogenation of 2-(acetylamino)-3-(4-fluorophenyl)propenoic methyl ester with **3d** was too slow to allow comparison of the corresponding *ee* value with that obtained with the faster catalyst **4a**.

Finally, we found that by using equimolar mixtures of (R_{Bn},R_{bin})-**3b** and (S_{Bn},R_{bin})-**3d** in the hydrogenation of 2-(acetylamino)-3-(phenyl)propenoic methyl ester did not significantly modify the *ee* (Table 1, Entry 31), although in this experiment the activity unexpectedly dropped. Similar observations were made by using the (S_{Bn},R_{bin})-**3d**/(S_{Me},R_{bin})-**4a** couple (Table 1, Entry 32). Thus, these results contrast the recent findings of Reetz et al. who showed that the combination of different phosphanes, in particular mixtures of chiral phosphites and *achiral* phosphanes, may produce a selectivity increase in hydrogenation experiments.[37]

Conclusions

In the present study we described the first monodentate P^{III} ligands combining a chiral 1,3-dioxa-2-phosphacycloheptadinaphthyl unit with a cost effective and readily available phenylalanine- or alanine-derived fragment. Despite their relative bulkiness, these ligands were found to readily form [$PtCl_2L_2$] complexes adopting a *cis* stereochemistry. When used in the rhodium-catalysed hydrogenation of prochiral olefins, the alanine–phosphoramidites displayed considerably higher hydrogenation rates than the sterically more crowded phenylalanine analogues. The highest enantioselectivities, 92%, were found with (R_{Bn},R_{bin})-**3b**. These are higher than those obtained with related, cheap phosphoramidites in which the amino group contains at least one stereogenic centre, but remain slightly below the performances of the "Feringa–de Vries" ligand **A** when used under similar conditions. Overall, this study confirms previous studies that have already established that the bulky, binoP moiety has a major impact on the enantioselectivity of hydrogenation reactions, overwhelming that of other stereogenic centres present in the molecule.

Experimental Section

General Procedures: All manipulations involving aminophosphanes and phosphoramidites were performed in Schlenk-type flasks under an atmosphere of dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. $CDCl_3$ was passed through a 5 cm-thick alumina column and stored under an atmosphere of nitrogen over molecular sieves (4 Å). Routine ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} spectra were recorded with Bruker FT Instruments (AC-200 and AC-300). ^{1}H NMR spectra were referenced to residual protonated solvents (δ = 7.26 ppm for $CDCl_3$ and 7.16 ppm for C_6D_6), ^{13}C chemical shifts are reported relative to deuterated solvents (δ = 77.16 ppm for $CDCl_3$ and 128.06 ppm for C_6D_6), and the ^{31}P NMR spectroscopic data are given relative to external H_3PO_4. Mass spectra were recorded with a Bruker MicroTOF spectrometer (ESI) and with CH_2Cl_2 as the solvent. Optical rotations were measured with a Perkin–Elmer 341 digital polarimeter with a 1 dm cell. The ^{13}C{^{1}H} NMR assignments for (S_{Bn})-**2a** and (R_{Bn})-**2b** are partially based on a literature reference.[38] The chlorophosphite binoPCl was prepared according to a procedure described in the literature.[31]

Synthesis of Amino Esters

Methyl (*S*)-2-(Methylamino)-3-phenylpropionate [(S_{Bn})-1a]: A solution of methyl (*S*)-2-(benzyloxycarbonylmethylamino)-3-phenylpropionate (3.196 g, 9.732 mmol), in MeOH (100 mL) was treated with 10% Pd/C (0.320 g, 10 wt.-% equiv.) and H_2 (1 atm) at 30 °C. After stirring for 2 h, the reaction mixture was filtered through Celite, and the solvent was evaporated under vacuum to afford a colourless oil. Yield: 1.891 g, 100%. $[\alpha]_D^{20}$ = +25.6 (*c* = 0.30, $CHCl_3$) [ref.[38] $[\alpha]_D^{20}$ = +24.9 (*c* = 0.30, $CHCl_3$]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27–7.11 (m, 5 H, arom. H), 3.60 (s, 3 H, OCH_3), 3.42 [t, $^3J_{H,H}$ = 6.8 Hz, 1 H, HC(CO)], 2.91 (d, $^3J_{H,H}$ = 6.8 Hz, 2 H, PhCH_2), 2.32 (s, 3 H, NCH_3), 1.76 (s, 1 H, N*H*CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.49 (s, C=O), 137.04 (s, quat. C), 128.96 (s, arom. CH), 128.74 (s, arom. CH), 128.31 (s, arom. CH), 128.00 (s, arom. CH), 126.59 (s, arom. CH), 64.47 [s, H*C*(CO)], 51.42 (s, OCH_3), 39.26 (s, Ph*C*H_2), 34.52 (s, NCH_3) ppm. $C_{11}H_{15}NO_2$ (193.24): calcd. C 68.4, H 7.8, N 7.3; found C 68.6, H 7.8, N 7.3.

Methyl (*R*)-2-(Methylamino)-3-phenylpropionate [(R_{Bn})-1b]: (R_{Bn})-**1b** was prepared according to the above procedure from methyl (*R*)-2-(benzyloxycarbonylmethylamino)-3-phenylpropionate (5.240 g, 15.96 mmol). Yield: 3.100 g, 100%. $[\alpha]_D^{20}$ = –25.5 (*c* = 1.00, $CHCl_3$) [ref.[38] $[\alpha]_D^{20}$ = –25.1 (*c* = 1.00, $CHCl_3$)]. $C_{11}H_{15}NO_2$ (193.24): calcd. C 68.4, H 7.8, N 7.3; found C 68.3, H, 7.9, N 7.4.

Methyl (*S*)-2-(Methylamino)propionate Monohydrochloride {[(S_{Me})-1c]HCl}: Thionyl chloride (1.300 g, 11.30 mmol, ca. 0.83 mL) was added dropwise to MeOH (15 mL) at 0 °C. To this mixture was added a solution of (*S*)-2-(methylamino)propionic acid (0.400 g, 3.80 mmol) in MeOH (10 mL). After stirring at r.t. for 4 d, the solvent was evaporated to dryness in vacuo to afford the product as a white solid. Yield: 0.600 g, 100%. $[\alpha]_D^{20}$ = +0.5 (*c* = 2.00, EtOH) [ref.[39] $[\alpha]_D^{20}$ = +1.0 (*c* = 2.00, EtOH)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.06 (br., 1 H, N*H*), 3.94 [d, $^3J_{H,H}$ = 6.9 Hz, 1 H, HC(CO)], 3.84 (s, 3 H, OC*H*$_3$), 2.79 (s, 3 H, NCH_3), 1.73 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CHC*H*$_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.09 (s, *C*=O), 56.20 [s, H*C*(CO)], 53.46 (s, OCH_3), 30.88 (s, NCH_3), 14.49 (s, CH*C*H_3) ppm. $C_5H_{12}ClNO_2$ (153.61): calcd. C 39.1, H 7.9, N 9.1; found C 39.2, H 7.8, N 9.1.

Methyl (*S*)-2-(Methyldiphenylphosphanylamino)-3-phenylpropionate [(S_{Bn})-2a]: To a solution of (S_{Bn})-**1a** (2.110 g, 10.86 mmol) in toluene (30 mL) was added successively diisopropylethylamine (1.404 g, 13.90 mmol, ca. 1.88 mL) and chlorodiphenylphosphane (2.397 g, 10.86 mmol, ca. 1.95 mL). The mixture was stirred overnight at r.t., then filtered through Al_2O_3. The solvent was evaporated to dryness, after which the residue was purified by flash chromatography over silica (cyclohexane/ethyl acetate, 70:30). Product (S_{Bn})-**2a** was obtained as a white solid. Yield: 3.510 g, 86%. M.p. 72–74 °C. $[\alpha]_D^{20}$ = –84.3 (*c* = 1.00, toluene). ^{1}H NMR (300 MHz, C_6D_6): δ = 7.50–7.44 (m, 2 H, arom. H), 7.18–6.99 (m, 13 H, arom. H), 4.51 [ddd, $J_{H,H}$ = 6.2 Hz, $J_{H,H}$ = 9.8 Hz, $J_{H,P}$ = 11.6 Hz, 1 H, HC(CO)], 3.22 (s, 3 H, OCH_3), 3.23 and 3.02 (ABX spectrum, $^2J_{A,B}$ = 14.3 Hz, $^3J_{A,X}$ = 6.2 Hz, $^3J_{B,X}$ = 9.8 Hz, 2 H, PhC*H*$_2$), 2.43 (d, $^3J_{HP}$ = 2.6 Hz, 3 H, NCH_3) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 172.74 (d, $^3J_{C,P}$ = 3.1 Hz, *C*=O), 139.44 (d, $^1J_{C,P}$ = 16.2 Hz, quat. C of PPh_2), 139.28 (d, $^1J_{C,P}$ = 11.8 Hz, quat. C of PPh_2), 138.46 (s, quat. C of benzyl), 132.76 (d, $J_{C,P}$ = 20.5 Hz, arom. CH of PPh_2), 132.65 (d, $J_{C,P}$ = 19.9 Hz, arom. CH of PPh_2), 129.65 (s, arom. CH of benzyl), 128.83 (s, arom. CH of benzyl), 128.54 (d, $J_{C,P}$ = 11.8 Hz, arom. CH of PPh_2), 128.28 (s, arom. CH), 128.27 (d, $J_{C,P}$ = 8.8 Hz, arom. CH of PPh_2), 128.25 (s, arom. CH), 126.66 (s, arom. CH), 69.32 [d, $^2J_{C,P}$ = 40.3 Hz, *C*(CO)], 50.96 (s, OCH_3), 36.77 (d, $^3J_{C,P}$ = 9.3 Hz, $PhCH_2$), 32.57 (d, $^2J_{C,P}$ = 8.7 Hz, NCH_3) ppm. ^{31}P NMR (121 MHz, C_6D_6): δ = 67.9 (s) ppm. MS (ESI-TOF): *m*/*z* (%) = 378.18 (88) [M + H]$^+$. $C_{23}H_{24}NO_2P$ (377.42): calcd. C 73.2, H 6.4, N 3.7; found C 73.1, H 6.5, N 3.6.

Methyl (*R*)-2-(Methyldiphenylphosphanylamino)-3-phenylpropionate [(R_{Bn})-2b]: Compound (R_{Bn})-**2b** was prepared according to the above procedure from (R_{Bn})-**1b** (2.480 g, 12.77 mmol). Yield: 4.240 g, 88%. $[\alpha]_D^{20}$ = +85.2 (*c* = 1.00, toluene). MS (ESI-TOF): *m*/*z* (%) = 378.18 (100) [M + H]$^+$. $C_{23}H_{24}NO_2P$ (377.42): calcd. C 73.2, H 6.4, N 3.7; found C 73.1, H 6.5, N 3.6.

General Procedure for the Synthesis of Phosphoramidites 3 and 4: To a solution of $MeNHCHR(CO_2Me)$ (R = CH_2Ph, Me) in toluene (30 mL) was added diisopropylethylamine (1 equiv.) and chloro-(*S* or *R*)-2,2′-*O*,*O*′-(1,1′-binaphthyl)phosphite (1 equiv.). The mixture was stirred overnight at r.t. before being filtered through Al_2O_3. The solvent was removed in vacuo to afford the product as a white solid.

Methyl (*S*)-2-{*N*,*N*-Methyl-[(*S*)-(dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yl)]amino}-3-phenylpropionate [(S_{Bn},S_{bin})-3a]: Prepared according to the general procedure from (S_{Bn})-**1a** (1.000 g, 5.15 mmol), diisopropylethylamine (0.665 g, 5.15 mmol, ca. 0.89 mL) and chloro-(*S*)-2,2′-*O*,*O*′-(1,1′-binaphthyl)phosphite (1.806 g, 5.15 mmol). Yield: 1.502 g, 58%. M.p. 70–71 °C. $[\alpha]_D^{20}$ = +281.2 (*c* = 0.26, toluene). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95–7.73 (m, 4 H, arom. H), 7.48–7.15 (m, 12 H, arom. H), 6.66 (d, $J_{H,H}$ = 8.8 Hz, 1 H, arom. H), 4.53 [ddd, $^3J_{A,X}$ = 6.1 Hz, $^3J_{B,X}$ = 9.8 Hz, $^3J_{H,P}$ = 11.5 Hz, 1 H, HC(CO)], 3.76 (s, 3 H, OCH_3), 3.36 and 3.09 (ABX, $^2J_{A,B}$ = 14.4 Hz, $^3J_{A,X}$ = 6.1 Hz, $^3J_{B,X}$ = 9.8 Hz, 2 H, $PhCH_2$), 2.23 (d, $^3J_{HP}$ = 4.0 Hz, 3 H, NCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.41 (d, $^3J_{C,P}$ = 6.2 Hz, C=O), 149.67–122.10 (arom. C′s), 61.27 [d, $J_{C,P}$ = 43.4 Hz, H*C*(CO)], 52.35 (s, OCH_3), 35.51 (d, $J_{C,P}$ = 6.2 Hz, $PhCH_2$), 28.64 (s, NCH_3) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 149.0 (s) ppm. MS (ESI-TOF): *m*/*z* (%) = 530.16 (100) [M + Na]$^+$. $C_{31}H_{26}NO_4P$ (507.52): calcd. C 73.4, H 5.2, N 2.8; found C 73.5, H 5.3, N 2.6.

Methyl (*R*)-2-{*N*,*N*-Methyl-[(*R*)-(dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yl)]amino}-3-phenylpropionate [(R_{Bn},R_{bin})-3b]: Prepared according to the general procedure from (R_{Bn})-**2b** (1.560 g, 8.03 mmol), diisopropylethylamine (1.047 g, 8.10 mmol, ca. 1.40 mL) and chloro-(*R*)-2,2′-*O*,*O*′-(1,1′-binaphthyl)phosphite (2.840 g, 8.10 mmol). Yield: 2.703 g, 66%. $[\alpha]_D^{20}$ = –285.3 (*c* = 1.00, toluene). NMR as for (S_{Bn},S_{bin})-**3a**. MS (ESI-TOF): *m*/*z* (%) = 530.16 (100) [M + Na]$^+$. $C_{31}H_{26}NO_4P$ (507.52): calcd. C 73.4, H 5.2, N 2.8; found C 73.4, H 5.4, N 2.6.

Methyl (*R*)-2-{*N*,*N*-Methyl-[(*S*)-(dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yl)]amino}-3-phenylpropionate [(R_{Bn},S_{bin})-3c]: Prepared according to the general procedure from (R_{Bn})-**1b** (1.230 g, 6.33 mmol), diisopropylethylamine (0.818 g, 6.33 mmol, ca. 1.10 mL) and chloro-(*S*)-2,2′-*O*,*O*′-(1,1′-binaphthyl)phosphite (2.230 g, 6.33 mmol). Yield: 1.502 g, 58%. M.p. 70–71 °C. $[\alpha]_D^{20}$ = +542.6 (*c* = 1.00, toluene). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95–7.89 (m, 4 H, arom. H), 7.46–7.19 (m, 13 H, arom. H), 4.48 [ddd, $J_{A,X}$ = 5.5 Hz, $J_{B,X}$ = 10.0 Hz, $J_{H,P}$ = 11.6 Hz, 1 H, HC(CO)], 3.90 (s, 3 H, OCH_3), 3.29 and 3.01 (ABX, $J_{A,B}$ = 14.3 Hz, $J_{A,X}$ = 5.5 Hz, $J_{B,X}$ = 10.0 Hz, 2 H, $PhCH_2$), 2.26 (d, J_{HP} = 3.2 Hz, 3 H, NCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.46 (d, $^3J_{C,P}$ = 5.0 Hz, *C*=O), 150.15 (d, $J_{C,P}$ = 5.6 Hz, quat. C), 149.32 (s, quat. C), 137.43 (s, quat. C), 132.85 (d, $J_{C,P}$ = 1.2 Hz, quat. C), 132.63 (s, quat. C), 131.48 (s, quat. C), 130.90 (s, quat. C), 130.29 (s, arom. CH), 130.15 (s, arom. CH), 129.52 (d, $J_{C,P}$ = 1.2 Hz, arom. CH), 128.60 (s, 2 × arom. CH), 128.44 (s, arom. CH), 128.39 (s, arom. CH), 127.12 (s, arom. CH), 127.01 (s, arom. CH), 126.82 (s, arom. CH), 126.17 (s, 2 × arom. CH), 124.90 (s, arom. CH), 124.73 (s, arom. CH), 123.97 (d, $J_{C,P}$ = 5.0 Hz, quat. C), 122.67 (d, $J_{C,P}$ = 1.9 Hz, quat. C), 122.21 (s, arom. CH), 122.04 (s, arom. CH), 122.02 (s, arom. CH), 61.99 [d, $^2J_{C,P}$ = 45.3 Hz, H*C*(CO)], 52.33 (s, OCH_3), 34.96 (d, $^3J_{C,P}$ = 6.2 Hz, $PhCH_2$), 28.23 (d, $^2J_{C,P}$ = 3.7 Hz, NCH_3) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 148.6 (s) ppm. MS (ESI-TOF): *m*/*z* (%) = 530.16 (41) [M + Na]$^+$. $C_{31}H_{26}NO_4P$ (507.52): calcd. C 73.4, H 5.2, N 2.8; found C 73.3, H 5.2, N 2.6.

Methyl (*S*)-2-{*N*,*N*-Methyl-[(*R*)-(dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yl)]amino}-3-phenylpropionate [(S_{Bn},R_{bin})-3d]: Prepared according to the general procedure from (S_{Bn})-**1a** (1.897 g, 9.77 mmol), diisopropylethylamine (1.262 g, 9.77 mmol, ca. 1.69 mL) and chloro-(*R*)-2,2′-*O*,*O*′-(1,1′-binaphthyl)phosphite (3.440 g, 9.81 mmol). Yield: 3.400 g, 69%. $[\alpha]_D^{20}$ = –533.5 (*c* = 1.00, toluene). NMR as for (R_{Bn},S_{bin})-**3c**. MS (ESI-TOF): *m*/*z* (%) = 530.16 (100) [M + Na]$^+$. $C_{31}H_{26}NO_4P$ (507.52): calcd. C 73.4, H 5.2, N 2.8; found C 73.4, H 5.2, N 2.6.

Methyl (*S*)-2-{*N*,*N*-Methyl-[(*R*)-(dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yl)]amino}propionate [(S_{Me},R_{bin})-4a]: Prepared according to the general procedure from [(S_{Me})-**1c**]HCl (0.300 g, 1.95 mmol), diisopropylethylamine (0.530 g, 4.10 mmol, ca. 0.69 mL) and chloro-(*R*)-2,2′-*O*,*O*′-(1,1′-binaphthyl)phosphite (0.720 g, 2.05 mmol). Yield: 0.767 g, 91%. M.p. 62–64 °C. $[\alpha]_D^{20}$ = –475.8 (*c* = 0.85, toluene). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98–7.90 (m, 4 H, arom. H), 7.54 (d, $J_{H,H}$ = 8.8 Hz, 2 H, arom. H), 7.45–7.35 (m, 4 H, arom. H), 7.31–7.23 (m, 2 H, arom. H), 4.32 [dq, $^3J_{H,H}$ = 7.2 Hz, $^3J_{H,P}$ = 9.6 Hz, 1 H, HC(CO)], 3.84 (s, 3 H, OCH_3), 2.28 (d, $^3J_{H,P}$ = 4.8 Hz, 3 H, NCH_3), 1.42 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, CCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.43 (d, $^3J_{C,P}$ = 3.1 Hz, *C*=O), 150.08–122.04 (arom. C′s), 55.09 [d, $^2J_{C,P}$ = 42.2 Hz, H*C*(CO)], 52.22 (s, OCH_3), 28.10 (d, $^2J_{C,P}$ = 3.1 Hz, NCH_3), 16.08 (d, $^3J_{C,P}$ = 6.8 Hz, CCH_3) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 148.5 (s) ppm. MS (ESI-TOF): *m*/*z* (%) = 454.11 (91) [M + Na]$^+$. $C_{25}H_{22}NO_4P$ (431.42): calcd. C 69.6, H 5.1, N 3.3; found C 69.7, H 5.2, N 3.3.

Methyl (*S*)-2-{*N*,*N*-Methyl-[(*S*)-(dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yl)]amino}propionate [(S_{Me},S_{bin})-4b]: Prepared according to the general procedure from [(S_{Me})-**1c**]HCl (0.581 g, 3.78 mmol), diisopropylethylamine (1.026 g, 7.94 mmol, ca. 1.33 mL) and chloro-(*S*)-2,2′-*O*,*O*′-(1,1′-binaphthyl)phosphite (1.393 g, 3.97 mmol). Yield: 1.452 g, 89%. M.p. 61–63 °C. $[\alpha]_D^{20}$ = +481.2 (*c* = 0.85, toluene). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.97 (d, $J_{H,H}$ = 8.8 Hz, 1 H, arom. H), 7.93–7.87 (m, 3 H, arom. H), 7.53 (d, $J_{H,H}$ = 8.8 Hz, 1 H, arom. H), 7.44–7.38 (m, 4 H, arom. H), 7.34–7.21 (m, 3 H, arom. H), 4.24 [dq, $^3J_{H,H}$ = 7.2 Hz, $^3J_{H,P}$ = 9.9 Hz, 1 H, HC(CO)], 3.74 (s, 3 H, OCH_3), 2.33 (d, $^3J_{H,P}$ = 5.7 Hz, 3 H, NCH_3), 1.51 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, CCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.24 (d, $^3J_{CP}$ = 6.8 Hz, *C*=O), 149.80 (d, J_{CP} = 5.6 Hz, quat. C), 149.42 (s, quat. C), 132.89 (d, $J_{C,P}$ = 1.2 Hz, quat. C), 132.69 (s, quat. C), 131.54 (s, quat. C), 130.87 (s, quat. C), 130.44 (s, arom. CH), 130.02 (s, arom. CH), 128.46 (s, arom. CH), 128.36 (s, arom. CH), 127.12 (s, arom. CH), 127.07 (s, arom. CH), 126.22 (s, arom. CH), 124.96 (s, arom. CH), 124.78 (s, arom. CH), 124.01 (d, $J_{C,P}$ = 5.0 Hz, quat. C), 122.69 (d, $J_{C,P}$ = 1.9 Hz, quat. C), 122.12 (s, arom. CH), 122.09 (s, arom. CH), 122.07 (s, arom. CH), 55.14 [d, $^2J_{C,P}$ = 37.2 Hz, H*C*(CO)], 52.19 (s, OCH_3), 28.79 (d, $^3J_{C,P}$ = 6.8 Hz, CCH_3), 16.54 (d, $^2J_{C,P}$ = 6.2 Hz, NCH_3) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 148.2 (s) ppm. MS (ESI-

TOF): *m/z* (%) = 454.14 (87) [M + Na]$^+$. $C_{25}H_{22}NO_4P$ (431.42): calcd. C 69.6, H 5.1, N 3.3; found C 69.7, H 5.3, N 3.1.

Synthesis of Complexes

***cis*-Dichloridobis[methyl (*R*)-2-{*N*,*N*-methyl-[(*R*)-(dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yl)]amino}-3-phenylpropionate]-platinum(II) (5):** A solution of phosphoramidite (R_{Bn},R_{bin})-**3b** (0.250 g, 0.50 mmol) in CH_2Cl_2 (8 mL) was added to a solution of dichlorido(dicyclopentadienyl)platinum(II) (0.100 g, 0.25 mmol) in CH_2Cl_2 (10 mL). The solution was stirred at r.t. for 24 h. The solution was then concentrated to ca. 5 mL, after which *n*-pentane was added (30 mL). Cooling this solution down to –10 °C precipitated **5** as a white solid. Yield: 0.290 g, 91%. M.p. > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.35 (d, $J_{H,H}$ = 8.9 Hz, 1 H, arom. H), 8.12 (d, $J_{H,H}$ = 9.1 Hz, 1 H, arom. H), 7.98 (d, $J_{H,H}$ = 8.1 Hz, 1 H, arom. H), 7.91 (d, $J_{H,H}$ = 8.3 Hz, 1 H, arom. H), 7.71 (d, $J_{H,H}$ = 8.8 Hz, 1 H, arom. H), 7.52–7.42 (m, 3 H, arom. H), 7.36–7.32 (m, 2 H, arom. H), 7.03 (t, $J_{H,H}$ = 7.5 Hz, 1 H, arom. H), 6.74 (t, $J_{H,H}$ = 7.7 Hz, 2 H, arom. H), 6.63 (d, $J_{H,H}$ = 7.3 Hz, 2 H, arom. H), 6.36 (d, $J_{H,H}$ = 8.8 Hz, 1 H, arom. H), 4.12 [ddd, $^3J_{H,H}$ = 8.6 Hz, $^3J_{H,H}$ = 6.8 Hz, $^3J_{H,P}$ = 11.3 Hz, 1 H, HC(CO)], 3.41 (s, 3 H, OCH_3), 2.65 and 2.37 (ABX, $^2J_{A,B}$ = 14.3 Hz, $^3J_{A,X}$ = 8.6 Hz, $^3J_{B,X}$ = 6.8 Hz, 2 H, $PhCH_2$), 2.24 (d, $^3J_{H,P}$ = 10.4 Hz, 3 H, NCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.13 (s, *C*=O), 148.11 (virtual t, $^3J_{C,P}$ + $^5J_{C,P'}$ = 3.7 Hz, quat. C), 147.93 (d, $J_{C,P}$ = 6.2 Hz, quat. C), 136.13 (s, quat. C), 132.25 (s, quat. C), 131.90 (s, quat. C), 131.77 (s, quat. C), 131.46 (s, quat. C), 131.42 (s, arom. CH), 130.65 (s, arom. CH), 129.24 (s, arom. CH), 128.70 (s, arom. CH), 128.43 (s, arom. CH), 128.20 (s, arom. CH), 127.27 (s, arom. CH), 126.97 (s, arom. CH), 126.73 (s, arom. CH), 126.50 (s, arom. CH), 126.04 (s, arom. CH), 125.77 (s, arom. CH), 123.19 (s, arom. CH), 122.59 (s, quat. C), 122.19 (s, quat. C), 120.51 (s, arom. CH), 59.75 [virtual t, $^2J_{C,P}$ + $^4J_{C,P'}$ = 6.5 Hz, H*C*(CO)], 51.80 (s, OCH_3), 35.78 (s, Ph*C*H$_2$), 30.93 (virtual t, $^2J_{C,P}$ + $^4J_{C,P'}$ = 2.5 Hz, NCH_3) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 94.9 ($J_{Pt,P}$ = 5578 Hz) ppm MS (ESI-TOF): *m/z* (%) = 1244.17 (61) [M – Cl]$^+$. $C_{62}H_{52}Cl_2N_2O_8P_2Pt$ (1281.02): calcd. C 58.2, H 4.0, N 2.0; found C 58.0, H 4.2, N 2.0.

***cis*-Dichloridobis[methyl (*S*)-2-{*N*,*N*-methyl-[(*R*)-(dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yl)]amino}-3-phenylpropionate]-platinum(II) (6):** A solution of phosphoramidite (S_{Bn},R_{bin})-**3d** (0.110 g, 0.22 mmol) in CH_2Cl_2 (8 mL) was added to a solution of [PtCl$_2$(cod)] (0.040 g, 0.11 mmol) in CH_2Cl_2 (10 mL). After stirring for 24 h, the solution was concentrated to 6 mL, after which *n*-pentane (30 mL) was added. Cooling the solution down to –10 °C afforded **6** as a white solid. Yield: 0.130 g, 95%. M.p. > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.34 (d, $J_{H,H}$ = 8.9 Hz, 1 H, arom. H), 8.12 (d, $J_{H,H}$ = 9.1 Hz, 1 H, arom. H), 7.98 (d, $J_{H,H}$ = 8.1 Hz, 1 H, arom. H), 7.89 (d, $J_{H,H}$ = 8.9 Hz, 1 H, arom. H), 7.69 (d, $J_{H,H}$ = 8.9 Hz, 1 H, arom. H), 7.47 (m, 3 H, arom. H), 7.35 (m, 2 H, arom. H), 7.17 (m, 1 H, arom. H), 7.01 (t, $J_{H,H}$ = 7.4 Hz, 1 H, arom. H), 6.73 (t, $J_{H,H}$ = 7.7 Hz, 2 H, arom. H), 6.62 (d, $J_{H,H}$ = 6.9 Hz, 2 H, arom. H), 6.36 (d, $J_{H,H}$ = 8.8 Hz, 1 H, arom. H), 4.11 [ddd, $^3J_{H,H}$ = 8.6 Hz, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,P}$ = 11.3 Hz, 1 H, HC(CO)], 3.39 (s, 3 H, OCH_3), 2.65 and 2.37 (ABX, $^2J_{A,B}$ = 14.2 Hz, $^3J_{A,X}$ = 8.6 Hz, $^3J_{B,X}$ = 6.9 Hz, 2 H, CH_2Ph), 2.22 (d, $^3J_{HP}$ = 10.9 Hz, 3 H, NCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.97 (virtual t, $^3J_{C,P}$ + $^5J_{C,P'}$ = 7.4 Hz, C=O), 148.37 (virtual t, $^3J_{C,P}$ + $^5J_{C,P'}$ = 12.4 Hz, quat. C), 147.82 (virtual t, $^3J_{C,P}$ + $^5J_{C,P'}$ = 6.8 Hz, quat. C), 137.38 (s, 2 × quat. C), 132.41 (s, quat. C), 131.67 (d, $J_{C,P}$ = 0.6 Hz, quat. C), 131.60 (s, arom. CH), 130.96 (s, arom. CH), 130.44 (s, arom. CH), 129.23 (d, $J_{C,P}$ = 0.6 Hz, arom. CH), 128.53 (d, $J_{C,P}$ = 0.6 Hz, arom. CH), 128.39 (d, $J_{C,P}$ = 0.6 Hz, arom. CH), 127.47 (d, $J_{C,P}$ = 0.6 Hz, arom. CH), 127.06 (s, arom. CH), 126.55 (d, $J_{C,P}$ = 0.6 Hz, arom. CH), 126.48 (s, arom. CH), 126.30 (d, $J_{C,P}$ = 0.6 Hz, arom. CH), 126.11 (d, $J_{C,P}$ = 0.6 Hz, arom. CH), 125.36 (s, arom. CH), 122.88 (d, $J_{C,P}$ = 1.2 Hz, 2 × quat. C), 122.19 (s, arom. CH), 122.01 (s, quat. C), 120.45 (s, arom. CH), 51.86 [virtual t, $^2J_{C,P}$ + $^4J_{C,P'}$ = 21 Hz, H*C*(CO)], 51.71 (s, OCH_3), 35.37 (d, $^3J_{C,P}$ = 1.9 Hz, Ph*C*H$_2$), 31.07 (s, NCH_3) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 95.0 ($J_{Pt,P}$ = 5579 Hz) ppm. MS (ESI-TOF): *m/z* (%) = 1244.25 (12) [M – Cl]$^+$. $C_{62}H_{52}Cl_2N_2O_8P_2Pt$ (1281.02): calcd. C 58.2, H 4.0, N 2.0; found C 58.0, H 4.2, N 2.0.

X-ray Crystal Structure Determination of 5: Crystals of **5** suitable for X-ray diffraction were obtained by slow diffusion of pentane into a chloroform solution of the complex. $2(C_{62}H_{52}Cl_2N_2O_8Pt)\cdot 2(0.5CHCl_3)\cdot 0.5C_5H_{12}$, M = 2717.41, tetragonal, $P4_1$, a = b = 11.5731(2) Å, c = 89.444(2) Å, V = 11979.8(4) Å^3, Z = 4, $D_{calcd.}$ = 1.507 g cm^{-3}, λ(Mo-K_α) = 0.71073 Å, μ = 26.08 cm^{-1}, F(000) = 5468, T = 100 K. The sample (0.25 × 0.20 × 0.20 mm) was studied with a Bruker AXS X8-APEX II diffractometer with graphite monochromatized Mo-K_α radiation. Data collection was carried out by using the Bruker collect suite.[40] 51864 Reflections were collected ($1.76 < \theta < 27.54°$), of which 20757 had $I > 2.0\sigma(I)$. The structure was solved with SIR-97,[41] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms could be localized on Fourier difference map. The whole structure was refined with SHELXL-97.[42] Hydrogen atoms were included and refined by using a riding mode in SHELX-97. Final results: R_1 = 0.065, wR_2 = 0.152, goodness of fit 1.135, 1465 parameters, residual electron density: min/max = –2.47/1.89. Flack parameter: 0.064(7).

Crystal Data for 6: Crystals of **6** suitable for X-ray diffraction were obtained by slow diffusion of pentane into a dichloromethane solution of the complex. $PtCl_2P_2C_{62}H_{52}O_8N_2\cdot 3H_2O$, M = 1335.03, orthorhombic, space group $P2_12_12_1$, a = 9.9546(3) Å, b = 26.5366(9) Å, c = 26.8868(9) Å, V = 7102.5(4) Å^3, Z = 4, $D_{calcd.}$ = 1.249 g cm^{-3}, λ(Mo-K_α) = 0.71073 Å, μ = 21.47 cm^{-1}, F(000) = 2696, T = 292(1) K. The sample (0.40 × 0.22 × 0.22 mm) was studied with an Oxford Diffraction Xcalibur Saphir 3 diffractometer with graphite monochromatized Mo-K_α radiation. The data collection was carried out by using CrysAlis RED.[43] 22955 Reflections collected ($1.76 < \theta < 27.54°$), 7763 observations with $I > 2.0\sigma(I)$. The structure was solved with SIR-97,[41] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms could be localized with a Fourier difference. The whole structure was refined with SHELXL97.[42] Hydrogen atoms were included and refined by using a riding mode in SHELX-97. Final results: R_1 = 0.060, wR_2 = 0.165, goodness of fit 0.917, 722 parameters, residual electron density: min/max = –0.957/1.526. Flack parameter: 0.069(10).

CCDC-613420 and -286303 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.

General Procedure for Asymmetric Hydrogenation and Determination of Enantiomeric Excesses: To a solution of [Rh(cod)$_2$]BF$_4$ (0.010 g, 0.025 mmol) in CH_2Cl_2 (10 mL) was added a solution of the ligand (2.2 equiv.) in CH_2Cl_2 (10 mL), and the resulting mixture was stirred for 30 min. before being used in the catalytic run. For those runs carried out with another solvent, the previous solution was evaporated to dryness; the residue was then dissolved in the desired solvent (20 mL). The solution was introduced by syringe into a 100-mL glass-lined, stainless steel autoclave containing a magnetic stirring bar and the substrate (2.5 mmol); the autoclave was then placed under an atmosphere of hydrogen (5 bar). At the end of the catalytic run, the autoclave was depressurized and the mixture was passed through a short silica column to remove the catalyst. Conversions were monitored by ^1H NMR spectroscopy. Enantioselectivities were determined by chiral GC analysis by using a CHROMPAK chiral fused silica 25 m × 0.25 mm i.d. and/or specific rotation. Coating Chirasil-L-Val column.

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[1] E. Cesarotti, G. D'Alfonso, *Tetrahedron Lett.* **1982**, *23*, 2995–2996.

[2] E. Cesarotti, G. Ciani, A. Sironi, *J. Organomet. Chem.* **1983**, *251*, 79–91.

[3] G. Pracejus, H. Pracejus, *J. Mol. Catal.* **1984**, *24*, 227–230.

[4] E. Cesarotti, L. Prati, *Gazz. Chim. Ital.* **1987**, *117*, 129–133.

[5] E. Cesarotti, S. Araneo, I. Rimoldi, S. Tassi, *J. Mol. Catal. A* **2003**, *204–205*, 211–220.

[6] M. Petit, A. Mortreux, F. Petit, G. Buono, G. Peiffer, *New J. Chem.* **1983**, *7*, 593–596.

[7] A. Karim, A. Mortreux, F. Petit, G. Buono, G. Peiffer, C. Siv, *J. Organomet. Chem.* **1986**, *317*, 93–104.

[8] C. Hatat, A. Karim, N. Kokel, A. Mortreux, F. Petit, *New J. Chem.* **1990**, *14*, 141–152.

[9] F. Hapiot, F. Agbossou, A. Mortreux, *Tetrahedron: Asymmetry* **1995**, *6*, 11–14.

[10] C. Döbler, U. Schmidt, H. W. Krause, H. J. Kreuzfeld, M. Michalik, *Tetrahedron: Asymmetry* **1995**, *6*, 385–388.

[11] A. Roucoux, L. Thieffry, J. F. Carpentier, M. Devocelle, C. Méliet, F. Agbossou, A. Mortreux, *Organometallics* **1996**, *15*, 2440–2449.

[12] M. Devocelle, F. Agbossou, A. Mortreux, *Synlett* **1997**, 1306–1308.

[13] C. Pasquier, J. Eilers, I. Reiners, J. Martens, A. Mortreux, F. Agbossou, *Synlett* **1998**, 1162–1164.

[14] E. A. Broger, W. Burkart, M. Hennig, M. Scalone, R. Schmid, *Tetrahedron: Asymmetry* **1998**, *9*, 4043–4054.

[15] F. Agbossou, J.-F. Carpentier, F. Hapiot, I. Suisse, A. Mortreux, *Coord. Chem. Rev.* **1998**, *178–180*, 1615–1645.

[16] V. Turcry, C. Pasquier, F. Agbossou-Niedercorn, *C. R. Acad. Sci.* **2003**, *6*, 179–184.

[17] F. Agbossou-Niedercorn, I. Suisse, *Coord. Chem. Rev.* **2003**, *242*, 145–158.

[18] N. V. Dubrovina, V. I. Tararov, Z. Kadyrova, A. Monsees, A. Börner, *Synthesis* **2004**, *12*, 2047–2051.

[19] M. van den Berg, R. M. Haak, A. J. Minnaard, A. H. M. de Vries, J. G. de Vries, B. L. Feringa, *Adv. Synth. Catal.* **2002**, *344*, 1003–1007.

[20] A.-G. Hu, Y. Fu, J.-H. Xie, H. Zhou, L.-X. Wang, Q.-L. Zhou, *Angew. Chem. Int. Ed.* **2002**, *41*, 2348–2350.

[21] X. Jia, X. Li, L. Xu, Q. Shi, X. Yao, A. S. C. Chan, *J. Org. Chem.* **2003**, *68*, 4539–4541.

[22] D. Peña, A. J. Minnaard, J. A. F. Boogers, A. H. M. de Vries, J. G. de Vries, B. L. Feringa, *Org. Biomol. Chem.* **2003**, *1*, 1087–1089.

[23] L. Lefort, J. A. F. Boogers, A. H. M. de Vries, J. G. de Vries, *Org. Lett.* **2004**, *6*, 1733–1735.

[24] T. Jerphagnon, J. L. Renaud, C. Bruneau, *Tetrahedron: Asymmetry* **2004**, *15*, 2101–2111.

[25] H. Bernsmann, M. van den Berg, R. Hoen, A. J. Minnaard, G. Mehler, M. T. Reetz, J. G. de Vries, B. L. Feringa, *J. Org. Chem.* **2005**, *70*, 943–951.

[26] L. Panella, A. M. Aleixandre, G. J. Kruidhof, J. Robertus, B. L. Feringa, J. G. de Vries, A. J. Minnaard, *J. Org. Chem.* **2006**, *71*, 2026–2036.

[27] Q. H. Zeng, X. P. Hu, Z. C. Duan, X. M. Liang, Z. Zheng, *J. Org. Chem.* **2006**, *71*, 393–396.

[28] D. Peña, A. J. Minnaard, A. H. M. de Vries, J. G. de Vries, B. L. Feringa, *Org. Lett.* **2003**, *5*, 475–478.

[29] Q. H. Zeng, X. P. Ping Hu, X. M. Liang, Z. Zheng, *Chin. Chem. Lett.* **2005**, *16*, 1321–1323.

[30] A. M. Z. Slawin, J. D. Woollins, Q. Zhang, *Inorg. Chem. Commun.* **1999**, 386–388.

[31] R. Sablong, C. Newton, P. Dierkes, J. A. Osborn, *Tetrahedron Lett.* **1996**, *37*, 4933–4936.

[32] M. van den Berg, A. J. Minnaard, E. P. Schudde, J. van Esch, A. H. M. de Vries, J. G. de Vries, B. L. Feringa, *J. Am. Chem. Soc.* **2000**, *122*, 11539–11540.

[33] G. Francio, C. G. Arena, F. Faraone, C. Graiff, M. Lanfranchi, A. Tiripicchio, *Eur. J. Inorg. Chem.* **1999**, 1219–1227.

[34] J. Fawcett, E. G. Hope, A. M. Stuart, A. J. West, *Polyhedron* **2006**, *25*, 1182–1186.

[35] M. van den Berg, J. A. Minnaard, B. Feringa, G. J. de Vries, DE 601 23 093 T2 to DSM IP Assests, **2007**.

[36] Q.-H. Zeng, X.-P. Hu, Z.-C. Duan, X.-M. Liang, Z. Zheng, *J. Org. Chem.* **2006**, *71*, 393–396.

[37] M. T. Reetz, J.-A. Ma, R. Goddard, *Angew. Chem. Int. Ed.* **2005**, *44*, 412–415.

[38] J. D. Park, K. J. Lee, D. H. Kim, *Bioorg. Med. Chem.* **2001**, *9*, 237–243.

[39] J. Spengler, K. Burger, *Synthesis* **1998**, 67–70.

[40] *M. SMART Software* (Version 5.611) and *SAINT+* (Version 6.45), Bruker AXS, Wisconsin, USA.

[41] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1998**, *31*, 74–77.

[42] S. G. M. Sheldrick, *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

[43] *O.D.L. CrysAlis RED Software* (Version 1.171.29.9).

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