Monatshefte für Chemie 134, 1253–1269 (2003)
DOI 10.1007/s00706-003-0039-8

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Asymmetric Catalysis. Part 149 [1]. Synthesis of New Chiral Tridentate Ligands for Enantioselective Catalysis

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Received March 4, 2003; accepted March 4, 2003
Published online August 18, 2003

Summary. The synthesis of new chiral tridentate ligands is reported which coordinate transition metals in a meridional way. The ligands contain a pyridine ring, an oxazoline ring, and a strongly coordinating diphenylphosphanyl group. The methionine-derived ligand forms a copper complex, which has been studied by X-ray crystallography. The new ligands were tested in models of enantioselective catalyses, such as hydrogenation of ketopantolactone, hydrosilylation of acetophenone, and transfer hydrogenation of acetophenone.

Keywords. Tridentate ligands; Chirality; Enantioselective catalysis; X-ray structure analysis.

Introduction

In the beginning of enantioselective catalysis with transition metal compounds chiral monodentate ligands played a crucial role. Soon, however, chiral bidentate ligands took over [2]. Chiral tridentate ligands, which may coordinate the metal atom of a catalyst in a meridional or a facial way, have not been used extensively in enantioselective catalysis. In the present paper we describe series of chiral tridentate ligands which contain a pyridine ring, an oxazoline ring, rendered chiral by way of its aminoalcohol constituent, and a strongly coordinating diphenylphosphanyl group or a methylsulfanyl group [3]. The new ligands were tested in different models of enantioselective catalysis including hydrogenations, for which the diphenylphosphanyl group proved essential to activate molecular hydrogen [3].

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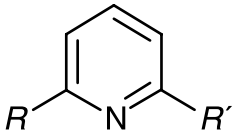
† X-ray structure analyses

Results and Discussion

Synthesis of Pyridine-Oxazoline Ligands with a $CH_2P(O)Ph_2$ Group as a Pyridine Substituent

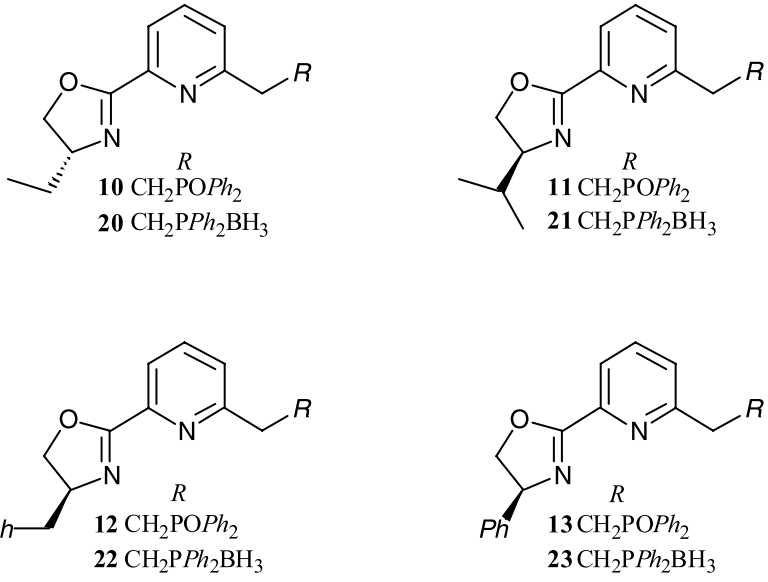
To synthesize pyridine derivatives with different substituents in 2,6-position, one of the two hydroxy groups of commercially available 2,6-(dihydroxymethyl)pyridine (**1**) had to be protected as a silyl ether. This was achieved by reaction with NaH followed by addition of $Ph_2{}^tBu$SiCl to give the monosilyl ether **2** in 77% yield [4]. The free hydroxy group in **2** was transformed into the tosylate leaving group in **3** with *Tos*Cl [5]. In the reaction with LiPPh_2 tosylate was replaced by diphenylphosphide. Subsequent oxidation with air gave the phosphanoyl derivative **4**. Deprotection of the silyl ether group in **5** was accomplished with Bu_4NF [6]. The free hydroxy group in **5** was oxidised to the aldehyde group in **6** by a *Swern* oxidation [7, 8]. Aldehyde **6** was converted into oxime **7** with hydroxylamine [9]. Addition of 1,1′-carbonyldiimidazol to **7** afforded the nitrile **8** [10], which was transformed into the carbomethoxyimidate **9** with NaO*Me* [11]. The precursors **1**–**9** are shown in Scheme 1.

The oxazoline rings in compounds **10**–**13** were built up in the reaction of **9** with the 2-aminoalcohols (*R*)-2-aminobutanol, (*S*)-valinol, (*S*)-phenylalaninol, and (*S*)-phenylglycinol (Scheme 2) [12]. Unfortunately, the phosphanoyl groups in these compounds could not be reduced to the phosphanyl functionality with $HSiCl_3$, which normally is used for such reductions [13, 14]. In these reactions diphenylphosphinic acid was cleaved off, characterised by ^{31}P NMR and X-ray crystallography [3].



	R	*R′*
1	CH_2OH	CH_2OH
2	$CH_2OSi^tBuPh_2$	CH_2OH
3	$CH_2OSi^tBuPh_2$	CH_2OTos
4	$CH_2OSi^tBuPh_2$	$CH_2P(O)Ph_2$
5	CH_2OH	$CH_2P(O)Ph_2$
6	CHO	$CH_2P(O)Ph_2$
7	CHNOH	$CH_2P(O)Ph_2$
8	CN	$CH_2P(O)Ph_2$
9	$C(NH)OCH_3$	$CH_2P(O)Ph_2$
14	$CH_2OSi^tBuPh_2$	$CH_2PPh_2BH_3$
15	CH_2OH	$CH_2PPh_2BH_3$
16	CHO	$CH_2PPh_2BH_3$
17	CHNOH	$CH_2PPh_2BH_3$
18	CN	$CH_2PPh_2BH_3$
19	$C(NH)OCH_3$	$CH_2PPh_2BH_3$

Scheme 1



Scheme 2

Synthesis of Pyridine-Oxazoline Ligands with a CH_2PPh_2 Group as a Pyridine Substituent

As the reduction of the phosphanoyl group in compounds **10**–**13** failed, oxidation of the phosphorus atom in the diphenylphosphanyl moiety must be prevented. A suitable protecting group for phosphorus in phosphanes is BH_3. By addition of BH_3·*THF* after the reaction of tosylate **3** with $LiPPh_2$, the phosphorus-protected product **14** was formed (Scheme 1) [15, 16]. A crystal structure proved the coordination of the BH_3 group to the phosphorus atom (Fig. 1). The following steps implying the intermediates **14**–**19** (Scheme 1) and the oxazoline derivatives **20**–**23** (Scheme 2) are analogous to those described above for the synthesis of **4**–**9** and **10**–**13**. The protecting BH_3 groups in **20**–**23** were removed by stirring with Et_2NH [17] yielding the target ligands **24**–**27** (Scheme 3), air-sensitive compounds even as solids.

The results of the catalytic reactions with ligands **24**–**27** did not meet the expectations (see below). An explanation could be the dissociation of the oxazoline nitrogen from the metal atom. Thus, the chiral centre would be too far away from the reaction centre to appreciably influence the formation of the product configuration. To avoid this dissociation, we tried to synthesize a pyridine-oxazoline ligand having the strongly coordinating diphenylphosphanyl group as a substituent directly on the oxazoline ring.

Synthesis of a Pyridine-Oxazoline Ligand with a CH_2PPh_2 Group as an Oxazoline Substituent

The synthesis of target ligands of type **32** started from the methyl ester of (*S*)-serine. Its derivatisation by introducing a *Boc* group at the nitrogen atom and by forming an oxazolidine ring on reaction with 2,2-dimethoxypropane as well as by

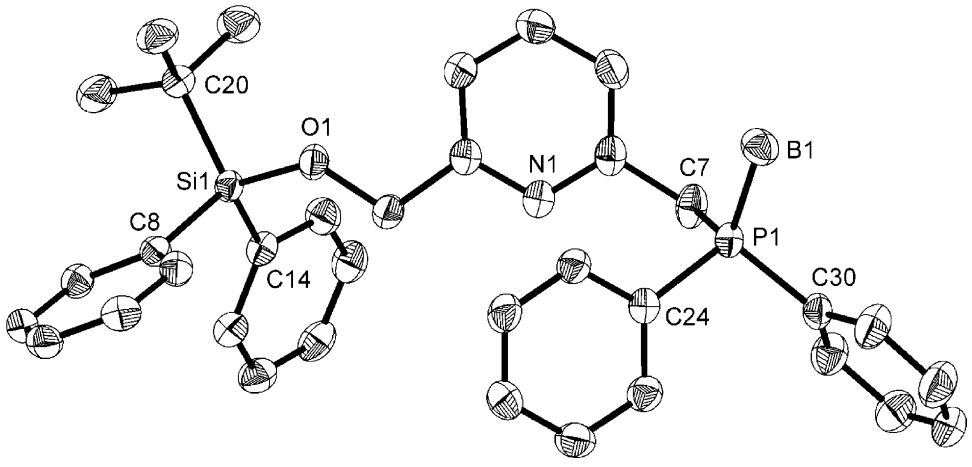
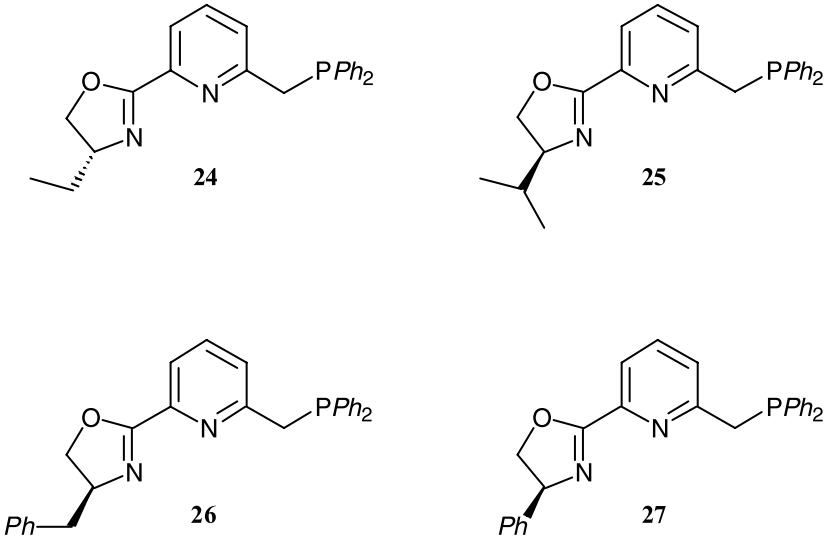
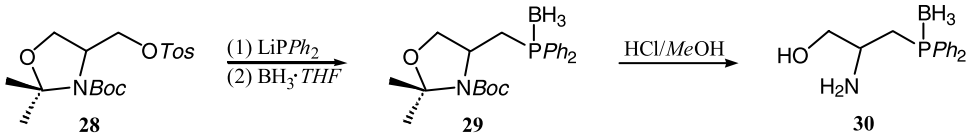


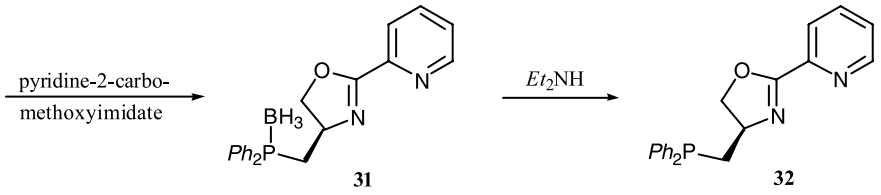
Fig. 1. View of **14** (H atoms omitted for clarity); selected bond lengths (Å) and angles (°): P1–C7 1.8303(18), P1–B1 1.914(2), Si1–O1 1.6482(12); C7–P1–C24 104.40(7), C7–P1–B1 112.25(9)



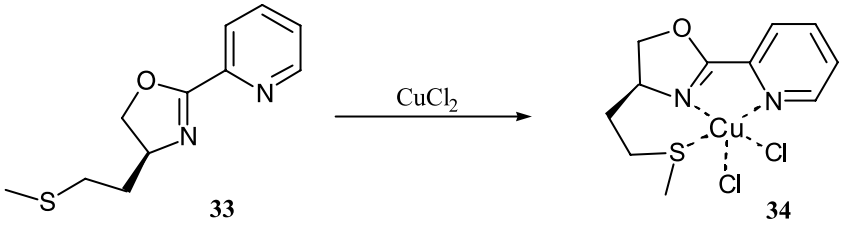
Scheme 3

reduction of the ester group to a primary alcoholic group and by transformation into the tosylate **28** has been reported [18]. Reaction of tosylate **28** with $LiPPh_2$ followed by addition of $BH_3{\cdot}THF$ and HCl cleavage of the oxazolidine ring in **29** has been mentioned in literature [19]. However, **29** and **30** (Scheme 4) have not been characterised. Therefore, they are included in the Experimental Part. The ring cleavage in **29** was achieved by stirring with *Me*OH saturated with HCl for 5 min [20]. Longer reaction times led to loss of the borane protecting group. The 2-aminoalcohol **30** was converted to the oxazoline **31** with pyridine-2-carbomethoxyimidate. The target ligand **32** (Scheme 4) was obtained by deprotection of the phosphorus with Et_2NH as described above.





Scheme 4



Scheme 5

Synthesis of the $CuCl_2$ Complex of a Pyridine-Oxazoline Ligand with a CH_2CH_2SMe Substituent

The tridentate ligands **24**–**27** and **32** should coordinate to a metal centre in a meridional way. With the carbon chain of the oxazoline substituent being longer, the ligand would have the possibility to lift its ''arm'' and coordinate facially to a metal centre. We tested this idea with ligand **33** synthesised starting from *L*-methionine *via* the aminoalcohol (*S*)-methioninol [12]. In methanol $CuCl_2$ and **33** gave crystals of the complex **34** (Scheme 5) suitable for X-ray analysis (Fig. 2). The coordination geometry at the copper atom is square pyramidal. The two chlorine atoms remain bonded. Ligand **33** coordinates meridionally to the copper atom.

Catalytic Hydrogenation of Ketopantolactone

In the enantioselective hydrogenation of ketopantolactone the procatalyst [Rh(*cod*)Cl]$_2$ was dissolved in 7 cm^3 of toluene or *THF*. The chiral ligand was dissolved in 1 cm^3 of the solvent (1.1-fold excess of ligand) and added. The colour changed from yellow to dark violet indicating complexation. After stirring the solution at room temperature for 30 min the reaction was started by addition of 200 equivalents of ketopantolactone. The hydrogenation was carried out at a hydrogen pressure of 50 bar and 50°C under careful exclusion of air [21, 22].

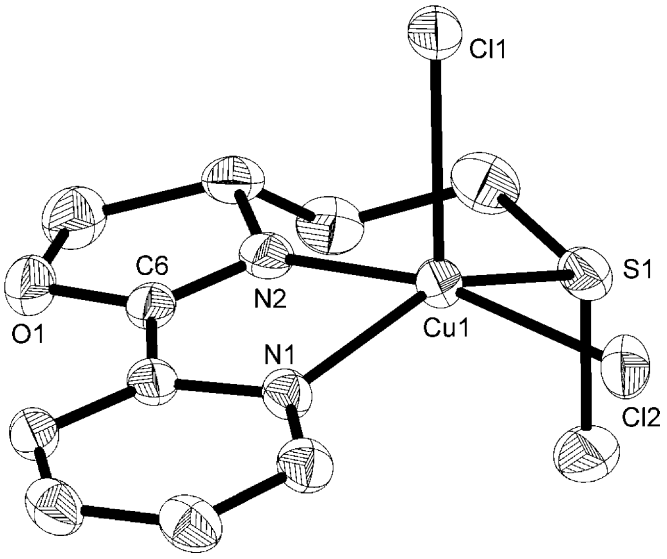
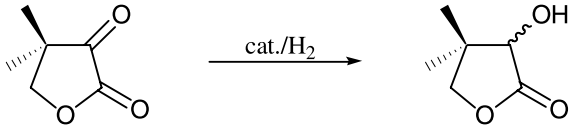


Fig. 2. View of **34** (H atoms omitted for clarity); selected bond lengths (Å) and angles (°): Cu1–S1 2.4085(7), Cu1–Cl1 2.4353(6), Cu1–N2 1.9700(17); N2–Cu1–S1 90.76(5), N1–Cu1–Cl2 94.01(5), Cl1–Cu1–Cl2 102.67(2)

Table 1. Enantioselective hydrogenation of ketopantolactone with *in situ* catalysts [Rh(*cod*)Cl]$_2$/**24**–**27** and **32**[a]



Procatalyst	Ligand	Solvent	Yield %[b]	*ee* %	Config.
[Rh(*cod*)Cl]$_2$	**24**	*THF*	18.2	4.1	(*S*)
[Rh(*cod*)Cl]$_2$	**25**	*THF*	3.1	<1.0	(*R*)
[Rh(*cod*)Cl]$_2$	**26**	*THF*	14.1	1.2	(*R*)
[Rh(*cod*)Cl]$_2$	**27**	*THF*	24.8	1.2	(*R*)
[Rh(*cod*)Cl]$_2$	**32**	*THF*	40.4	1.8	(*S*)
[Rh(*cod*)Cl]$_2$	**32**	toluene	36.5	17.1	(*S*)

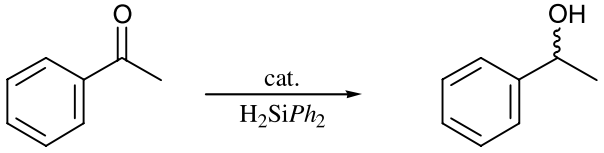
[a] Conditions: Rh:ligand:substrate = 1:1.1:200, $p = 50$ bar, $T = 50$°C, $t = 40$ h; work-up and enantiomer analysis see Ref. [22]; [b] yield of pantolactone

After a reaction time of 40 h the colour of the solution was still dark violet. The colour changed to yellow on contact with air. Table 1 shows that the hydrogenation yields are in the lower and middle area. The *in situ* catalyst [Rh(*cod*)Cl]$_2$/**32** afforded 36.3% yield and 17% *ee*.

Catalytic Hydrosilylation of Acetophenone

To the procatalyst [Rh(*cod*)Cl]$_2$ a 1.1-fold excess of a solution of the ligand in CH_2Cl_2 was added. The colour changed to dark violet. The solution was stirred at

Table 2. Enantioselective hydrosilylation of acetophenone with *in situ* catalysts [Rh(*cod*)Cl]$_2$/**24**–**27**, **32**, and **33**[a]



Procatalyst	Ligand	HS %[b]	EE %[c]	Yield %[d]	*ee* %	Config.
[Rh(*cod*)Cl]$_2$	**24**	86.0	9.0	78.3	<1.0	(*R*)
[Rh(*cod*)Cl]$_2$	**25**	86.9	6.4	81.4	<1.0	(*S*)
[Rh(*cod*)Cl]$_2$	**26**	85.2	10.2	76.5	<1.0	(*S*)
[Rh(*cod*)Cl]$_2$	**27**	84.6	14.7	72.2	6.9	(*R*)
[Rh(*cod*)Cl]$_2$	**32**	83.5	41.2	49.3	8.8	(*S*)
[Rh(*cod*)Cl]$_2$	**33**	76	47.9	39.6	<1.0	(*R*)

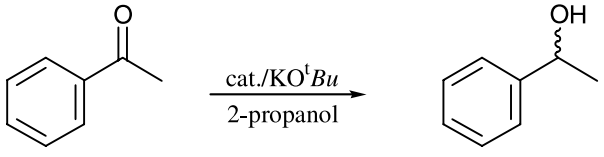
[a] Conditions: Rh:ligand:substrate:diphenylsilane = 1:1.1:400:400, $T = 0°C \rightarrow$ rt, $t = 24$ h; work-up and enantiomer analysis see Ref. [24]; [b] HS = hydrosilylation; [c] EE = enolether; [d] yield of 1-phenylethanol

room temperature for 30 min. Then the solvent was removed. The reaction was started by addition of acetophenone and diphenylsilane [23, 24]. Yields were good (Table 2), however, the enantiomeric excess was very low in all runs, except for ligand **27** (6.9% *ee*) and ligand **32** (8.8% *ee*).

Catalytic Hydrogenation of Acetophenone

After adding a 1.1-fold excess of ligand to the procatalyst [$RuCl_2(PPh_3)_3$] the 2-propanol solution was stirred at room temperature for 1 h. Then the substrate

Table 3. Enantioselective transfer hydrogenation of acetophenone with *in situ* catalysts [$RhCl_2(PPh_3)_3$]/**24**–**27**, **32**, and **33**[a]



Procatalyst	Ligand	Time h	Yield %[b]	*ee* %	Config.
[$RuCl_2(PPh_3)_3$]	**24**	15	15.9	10.8	(*R*)
[$RuCl_2(PPh_3)_3$]	**25**	15	4.3	9.0	(*S*)
[$RuCl_2(PPh_3)_3$]	**26**	15	20.6	6.7	(*S*)
[$RuCl_2(PPh_3)_3$]	**27**	15	15.2	1.3	(*S*)
[$RuCl_2(PPh_3)_3$]	**32**	15	1.8	34.2	(*S*)
[$RuCl_2(PPh_3)_3$]	**32**	72	2.8	38.1	(*S*)
[$RuCl_2(PPh_3)_3$]	**33**	15	1.9	15.1	(*R*)

[a] Conditions: Ru:ligand:substrate:KO^t*Bu* = 1:1.1:200:1, solvent 2-propanol, $T = 28°C$; work-up and enantiomer analysis see Ref. [26]; [b] yield of 1-phenylethanol

acetophenone (200-fold excess) and the base potassium-*tert*-butanolate were added [25, 26]. The results are shown in Table 3. The highest enantiomeric excess was 38% *ee* obtained with ligand **32**.

Experimental

Chromatography: Silica gel 60 (Merck). NMR spectra: Bruker AC 250, Bruker ARX 400 spectrometer. Mass spectra: Finnigan Mat 95 (FD and FAB), Finnigan 311A (EI), Thermoquest TSQ 7000 (ESI). The most intense peak is specified. Optical rotations: Perkin Elmer polarimeter 241.

(*R*)-(−)-2-Aminobutanol was commercially available. (*S*)-(+)-Valinol, (*S*)-(−)-phenylalaninol, (*S*)-(−)-phenylglycinol, and (*S*)-(+)-methioninol were obtained by reduction of the corresponding aminoacids [27]. (*S*)-*N-Boc*-2,2-dimethyl-4-tosyloxymethyloxazolidine **28** was synthesised as described starting from (*S*)-(+)-serine [18].

6-[(tert-Butyldiphenylsilyl)oxymethyl]-2-(hydroxymethyl)pyridine (**2**, $C_{23}H_{27}NO_2Si$)

To a suspension of 1.11 g of NaH (46.0 mmol) in 40 cm^3 of *THF* 5.85 g of 2,6-dihydroxymethylpyridine (**1**, 42.0 mmol), dissolved in 250 cm^3 of *THF*, were added at room temperature within 2 h under an atmosphere of dry N_2. A solution of 10.8 cm^3 of *tert*-butyldiphenylchlorosilane (42 mmol) in 5 cm^3 of *THF* was added dropwise with stirring at room temperature. The brown suspension was poured into a mixture of 165 cm^3 of diethyl ether and 22 cm^3 of a 10% Na_2CO_3 solution. The organic layer was dried (Na_2SO_4) and evaporated. The resulting pale yellow oil was chromatographed on a SiO_2 column (35 × 4 cm) with petroleum ether:ethyl acetate = 2:1. After the first fraction, consisting of the doubly silylated compound, the main fraction was **2** (colourless solid). The unprotected dialcohol **1** remained on the column. Yield 12.27 g (77%); mp 133°C; PI DCI MS: $m/z = 378$ (M, 100); ^{1}H NMR (250 MHz, $CDCl_3$, *TMS*): $\delta = 7.72$ (m, 5H, Ph, Py), 7.59 (d, $J = 7.4$ Hz, H^3-Py), 7.41 (m, 6H, Ph), 7.09 (d, $J = 7.6$ Hz, H^5-Py), 4.88 (s, CH_2OSi), 4.70 (d, $J = 4.8$ Hz, $C\underline{H}_2OH$), 3,71 (t, $J = 4.8$ Hz, $CH_2O\underline{H}$), 1.14 (s, $C(CH_3)_3$).

6-[(tert-Butyldiphenylsilyl)oxymethyl]-2-(tosyloxymethyl)pyridine (**3**, $C_{30}H_{33}NO_4Si$)

Powdered KOH (1.72 g, 30.7 mmol) was added to a solution of 7.18 g of **2** (19.0 mmol) in 30 cm^3 of *THF*. To this suspension a solution of 4.20 g of *Tos*Cl (22.0 mmol) in 15 cm^3 of *THF* was added dropwise at 0°C. The suspension was stirred for 5 h at 0°C and 12 h at room temperature. After filtration the residue was washed with a small amount of *THF* and the combined solutions were evaporated. The resulting solid was chromatographed (SiO_2, 40 × 6 cm) with petroleum ether:ethyl acetate = 7:1 to give **3** as a colourless solid. Yield 10.10 g (89%); mp 63–64°C; PI FD MS (CH_2Cl_2): $m/z = 474$ (M–$C(CH_3)_3$, 100); ^{1}H NMR (250 MHz, $CDCl_3$, *TMS*): $\delta = 7.71$ (m, 8H, Ph, Py), 7.34 (m, 9H, Ph, Py), 5.05 (s, CH_2OTos), 4.77 (s, CH_2OSi), 2.41 (s, CH_3), 1.12 (s, $C(CH_3)_3$).

2-[(tert-Butyldiphenylsilyl)oxymethyl]-6-[(diphenylphosphanoyl)methyl]pyridine
(**4**, $C_{35}H_{36}NO_2PSi$)

Under N_2 a solution of 3.50 g of **3** (6.58 mmol) in 50 cm^3 of *THF* was cooled to −50°C. An equimolar solution of Li*PPh*$_2$ (1 molar) in *THF* was added dropwise. Each drop was immediately decolourized. The resulting pale yellow solution was stirred for 1 h at −50°C and for 2 h at room temperature. Then the solution was stirred for 3 h on air. After removal of the solvent the residue was chromatographed (SiO_2, 35 × 4 cm) with CH_2Cl_2:methanol = 50:1 to afford **4** as a colourless solid. Yield 2.25 g (61%); PI FD MS (CH_2Cl_2): $m/z = 562$ (M, 4), 504 (M–$C(CH_3)_3$, 100); ^{1}H NMR (250 MHz, $CDCl_3$, *TMS*):

$\delta = 7.66$ (m, 9H, Ph, Py), 7.40 (m, 14H, Ph, Py), 4.66 (s, CH_2OSi), 3.84 (d, $J = 14.2$ Hz, CH_2P), 1.10 (s, $C(CH_3)_3$) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = 30.58$ (s, $POPh_2$) ppm.

6-(Diphenylphosphanoyl-κP-methyl)-2-(hydroxymethyl)pyridine (**5**, $C_{19}H_{18}NO_2P$)

Bu$_4$NF·3H_2O (1.61 g, 5.11 mmol) was added to a solution of 2.61 g of **4** (4.65 mmol) in 50 cm^3 of *THF*. The colour of the solution turned yellow. After stirring for 2 h at room temperature the solvent was evaporated and the residue was chromatographed (SiO_2, 25 × 3 cm) with CH_2Cl_2:methanol = 20:1 to give the colourless solid **5**. Yield 1.29 g (86%); mp 126°C; PI EI MS: $m/z = 323$ (M, 9), 201 (Ph_2PO, 73), 199 (M–Ph–CH_2OH, 100); ^1H NMR (400 MHz, $CDCl_3$, *TMS*): $\delta = 7.55$ (ddd, $J = 7.7$, 7.7, 0.4 Hz, H^4-Py), 7.52 (m, 3H, Ph), 7.45 (m, 7H, Ph), 7.66 (ddd, $J = 7.7$, 1.8, 0.9 Hz, 1H, $H^{3/5}$-Py), 7.73 (ddd, $J = 7.7$, 1.8, 0.9 Hz, 1H, $H^{3/5}$-Py), 4.54 (s, CH_2OH), 3.93 (d, $J = 14.0$ Hz, CH_2P), 3.60 (s, $CH_2O\underline{H}$) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = 30.60$ (s, $POPh_2$) ppm.

6-[(Diphenylphosphanoyl)methyl]pyridine-2-carbaldehyde (**6**, $C_{19}H_{16}NO_2P$)

Under N_2 a solution of 310 mm^3 of oxalyl chloride (3.61 mmol) in 8 cm^3 of CH_2Cl_2 was cooled to −80°C. A solution of 530 mm^3 of *DMSO* (7.46 mmol) in 2 cm^3 of CH_2Cl_2 was added dropwise such that gas evolution was not too vigorous. After 5 min a solution of 1.0 g of **5** (3.11 mmol) in 8 cm^3 of CH_2Cl_2 was added dropwise and stirred for 15 min at −80°C. After adding 2.20 cm^3 of *NE*t_3 (15.87 mmol) a brown precipitate formed immediately. The suspension was stirred while warming to room temperature. H_2O (16 cm^3) was added which dissolved the precipitate. The yellow-orange organic layer was washed twice with H_2O, dried (Na_2SO_4), and the solvent was evaporated. The residue was chromatographed (SiO_2, 25 × 3 cm) with dichloromethane:methanol = 30:1. The resulting **6** was obtained as a yellow solid. Yield 0.96 g (96%); mp 105°C; PI EI MS: $m/z = 321$ (M, 5), 201 ($POPh_2$, 100); ^1H NMR (400 MHz, $CDCl_3$, *TMS*): $\delta = 9.83$ (d, $J = 0.6$ Hz, CHO), 7.77 (m, 6H, Ph, Py), 7.58 (m, 7H, Ph, Py), 4.02 (d, $J = 13.9$ Hz, CH_2P) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = 30.32$ (s, $POPh_2$) ppm.

6-[(Diphenylphosphanoyl)methyl]pyridine-2-carbaldoxime (**7**, $C_{19}H_{17}N_2O_2P$)

H_2NOH·HCl (2.02 g, 29.1 mmol) was dissolved in 18 cm^3 of a 10% Na_2CO_3 solution and stirred until gas evolution stopped. This solution was added to a solution of 6.00 g of **6** (18.7 mmol) in 40 cm^3 of *Me*OH and stirred for 24 h at room temperature. After a few min a colourless precipitate formed. The suspension was concentrated and the precipitate was filtered off and washed with petroleum ether. The filtrate was evaporated and the residue was chromatographed (SiO_2, 25×3 cm) with CH_2Cl_2:methanol = 20:1. Compound **7** was obtained as a colourless solid. Yield 5.10 g (81%); mp 217–218°C; PI EI MS: $m/z = 336$ (M, 4), 318 (M–H_2O, 6), 201 ($POPh_2$, 100); ^1H NMR (400 MHz, *DMSO*-d_6, *TMS*): $\delta = 11.63$ (s, HCNO$\underline{H}$), 7.82 (m, 5H, Ph, $\underline{H}$CNOH), 7.67 (dd, $J = 7.7$, 7.7 Hz, H^4-Py), 7.53 (m, 7H, Ph, H^5-Py), 7.25 (ddd, $J = 7.7$, 1.9, 1.1 Hz, H^3-Py), 4.10 (d, $J = 11.9$ Hz, CH_2P) ppm; $^{31}P\{^1H\}$ NMR (*DMSO*-d_6, H_3PO_4 ext.): $\delta = 28.92$ (s, 1P, $POPh_2$) ppm.

6-[(Diphenylphosphanoyl)methyl]pyridine-2-carbonitrile (**8**, $C_{19}H_{15}N_2O_2P$)

To a solution of 2.0 g of **7** (6.2 mmol) in 70 cm^3 of dried *DMSO* 1.17 g of 1,1′-carbonyldiimidazol (7.2 mmol) were added. After stirring for 2 h at room temperature the solvent was evaporated. The residue was chromatographed (SiO_2, 25×3 cm) with CH_2Cl_2:methanol = 30:1. Compound **8** was obtained as a colourless solid. Yield 1.82 (92%); mp 147°C; PI EI MS: $m/z = 318$ (M, 15), 201 ($POPh_2$, 100); $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$, *TMS*): $\delta = 7.78$ (dd, $J =$ 8.0, 1.1 Hz, H^3-Py), 7.75 (m, 4H, Ph), 7.71 (dd, $J = 8.0$, 8.0 Hz, H^4-Py), 7.49 (m, 7H, Ph, H^5-Py), 3.96 (s, CH_2P) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = 30.39$ (s, $POPh_2$) ppm.

6-[(Diphenylphosphanoyl)methyl]pyridine-2-carbomethoxyimidate (**9**, $C_{20}H_{19}N_2O_2P$)

A solution of **8** (1.35 g, 3.9 mmol) in 80 cm^3 of *Me*OH was reacted with a solution of 0.096 g of sodium (4.2 mmol) in 10 cm^3 of MeOH under N_2. After stirring for 48 h at room temperature 280 mm^3 of glacial acetic acid (4.9 mmol) were added. The solvent was removed and the residue was dissolved in CH_2Cl_2. The solution was extracted twice with H_2O, the organic layer was dried over Na_2SO_4, and the solvent was evaporated to give **9** as a colourless solid. Yield 1.28 (94%); mp 176–177°C; PI EI MS: $m/z = 350$ (M, 2), 319 (M–OCH_3, 12), 201 ($POPh_2$, 100); ^{1}H NMR (250 MHz, $CDCl_3$, *TMS*): $\delta = 8.62$ (bs, NH), 7.79 (m, 4H, Ph), 7.68 (ddd, $J = 7.7$, 7.7, 0.5 Hz, H^4-Py), 7.61 (ddd, $J = 7.7$, 1.4, 1.3 Hz, H^5-Py), 7.50 (m, 7H, Ph, H^3-Py), 3.96 (d, $J = 14.0$ Hz, CH_2P), 3.93 (s, OCH_3) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = 30.57$ (s, $POPh_2$) ppm.

General Procedure for the Synthesis of Compounds **10–13** *from* **9** *with 2-Aminoalcohols*

9 was dissolved in *ca.* 30 cm^3 of chlorobenzene at 80°C. The corresponding 2-aminoalcohol (2.93 mmol) and one drop of conc. HCl as catalyst were added. N_2 was bubbled through the solution for 20 h to remove the compounds with low boiling points like *Me*OH or NH_3 displacing the equilibrium to the product side. After evaporating the solvent the residue was chromatographed (SiO_2, 20×3 cm) with CH_2Cl_2:methanol = 30:1.

(R)-2-[(Diphenylphosphanoyl)methyl]-6-(4-ethyl-4,5-dihydrooxazol-2-yl)pyridine
(**10**, $C_{23}H_{23}N_2O_2P$)

From (*R*)-(−)-2-aminobutanol as aminoalcohol. Colourless resin. Yield 1.05 g (94%); PI EI MS: $m/z = 390$ (M, 14), 361 (M–C_2H_5, 8), 201 (Ph_2PO, 100); $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$, *TMS*): $\delta = 7.85$ (ddd, $J = 7.6$, 1.3, 1.4 Hz, H^3-Py), 7.77 (m, 4H, Ph), 7.71 (ddd, $J = 7.8$, 1.3, 1.7 Hz, H^5-Py), 7.65 (dd, $J = 7.6$, 7.8 Hz, H^4-Py), 7.44 (m, 6H, Ph), 4.53 (dd, $J = 8.1$, 9.6 Hz, $OC\underline{H}^AH^BCHN$), 4.28 (m, $OCH^AH^BC\underline{H}N$), 4.11 (dd, $J = 8.1$, 8.1 Hz, $OCH^A\underline{H}^BCHN$), 4.06 (d, $J = 14.2$ Hz, $C\underline{H}^AH^BPO$), 4.05 (d, $J = 14.2$ Hz, $CH^A\underline{H}^BPO$), 1.79 (m, $C\underline{H}^AH^BCH_3$), 1.63 (m, $CH^A\underline{H}^BCH_3$), 1.00 (t, $J = 7.2$ Hz, $CH^AH^BC\underline{H}_3$) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = 30.50$ (s, $POPh_2$); IR (KBr): $\bar{\nu} = 1200$ (s) cm^{-1}; $[\alpha]_D = +37.0°\ cm^3\ g^{-1}\ dm^{-1}$ ($c = 1.0$, CH_2Cl_2).

(S)-2-[(Diphenylphosphanoyl)methyl]-6-(4-isopropyl-4,5-dihydrooxazol-2-yl)pyridine
(**11**, $C_{24}H_{25}N_2O_2P$)

From (*S*)-(+)-valinol as aminoalcohol. Colourless resin. Yield 0.80 g (69%); PI EI MS: $m/z = 404$ (M, 29), 361 (M–C_3H_7, 63), 201 (Ph_2PO, 100); $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$, *TMS*): $\delta = 7.86$ (ddd, $J = 7.5$, 1.5, 1.5 Hz, H^3-Py), 7.77 (m, 4H, Ph), 7.69 (ddd, $J = 7.8$, 1.5, 1.7 Hz, H^5-Py), 7.64 (dd, $J = 7.5$, 7.8 Hz, H^4-Py), 7.44 (m, 6H, Ph), 4.45 (dd, $J = 8.7$, 7.5 Hz, $OC\underline{H}^AH^BCHN$), 4.17 (m, $OCH^AH^BC\underline{H}N$), 4.07 (d, $J = 14.7$ Hz, $C\underline{H}^AH^BP$), 4.04 (d, $J = 14.7$ Hz, $CH^A\underline{H}^BP$), 1.90 (m, $C\underline{H}CH_3CH_3$), 1.02 (d, $J = 6.8$ Hz, $CHC\underline{H}_3CH_3$), 0.93 (d, $J = 6.7$ Hz, $CHCH_3C\underline{H}_3$) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = 30.51$ (s, $POPh_2$) ppm; IR (KBr): $\bar{\nu} = 1200$ (s) cm^{-1}; $[\alpha]_D = -40.0°\ cm^3\ g^{-1}\ dm^{-1}$ ($c = 1.0$, CH_2Cl_2).

(S)-2-[(Diphenylphosphanoyl)methyl]-6-(4-benzyl-4,5-dihydrooxazol-2-yl)pyridine
(**12**, $C_{28}H_{25}N_2O_2P$)

From (*S*)-(−)-phenylalaninol as aminoalcohol. Colourless solid. Yield 0.78 g (61%); mp 148–149°C; PI DCI MS: $m/z = 470$ (M + NH_4, 27), 453 (M, 100); $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$, *TMS*): $\delta = 7.85$ (dd, $J = 7.4$, 1.3 Hz, H^3-Py), 7.77 (m, 4H, Ph), 7.72 (dd, $J = 7.8$, 1.3 Hz, H^5-Py), 7.66 (dd, $J = 7.5$, 7.8 Hz, H^4-Py), 7.42 (m, 6H, Ph), 7.28 (m, 5H, Ph), 4.62 (m, $OCH^AH^BC\underline{H}N$), 4.40 (dd, $J = 8.6$,

9.4 Hz, OC$\underline{H}^{A}H^{B}$CHN), 4.19 (dd, $J = 8.6$, 7.6 Hz, OCH$^{A}\underline{H}^{B}$CHN), 4.08 (d, $J = 14.9$ Hz, C$\underline{H}^{A}H^{B}$P), 4.03 (d, $J = 14.9$ Hz, CH$^{A}\underline{H}^{B}$P), 3.27 (dd, $J = 13.7$, 5.0 Hz, C$\underline{H}^{A}H^{B}$Ph), 2.75 (dd, $J = 13.7$, 8.9 Hz, CH$^{A}\underline{H}^{B}$Ph) ppm; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = 30.48$ (s, $POPh_2$) ppm; IR (KBr): $\bar{\nu} = 1190$ (s) cm^{-1}; $[\alpha]_D = -20.0°\ cm^3\,g^{-1}\,dm^{-1}$ ($c = 1.0$, CH_2Cl_2).

(S)-2-[(Diphenylphosphanoyl)methyl]-6-(4-phenyl-4,5-dihydrooxazol-2-yl)pyridine (**13**, $C_{27}H_{23}N_2O_2P$)

From (*S*)-(−)-phenylglycinol as 2-aminoalcohol. Colourless resin. Yield 0.50 (40%); LT PI LSI MS: $m/z = 439$ (M, 100); $^{1}H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$, *TMS*): $\delta = 7.94$ (dd, $J = 7.3$, 1.5 Hz, H^3-Py), 7.78 (m, 4H, Ph), 7.72 (dd, $J = 7.8$, 1.5 Hz, H^5-Py), 7.68 (dd, $J = 7.3$, 7.8 Hz, H^4-Py), 7.39 (m, 11H, Ph), 5.41 (dd, $J = 10.1$, 8.3 Hz, OCH^{A}H^{B}C$\underline{H}$N), 4.84 (dd, $J = 10.1$, 8.5 Hz, OC$\underline{H}^{A}$H^{B}CHN), 4.34 (dd, $J = 8.3$, 8.5 Hz, OCH$^{A}\underline{H}^{B}$CHN), 4.10 (d, $J = 14.7$ Hz, C$\underline{H}^{A}$H^{B}P), 4.04 (d, $J = 14.7$ Hz, CH$^{A}\underline{H}^{B}$P) ppm; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = 30.56$ (s, $POPh_2$) ppm; IR (KBr): $\bar{\nu} = 1190$ (s) cm^{-1}; $[\alpha]_D = +54.0°\ cm^3\,g^{-1}\,dm^{-1}$ ($c = 1.0$, CH_2Cl_2).

Trihydroborane[2-[(tert-butyldiphenylsilyl)oxymethyl]-6-(diphenylphosphanyl-κP-methyl)pyridine] (**14**, $C_{35}H_{39}BNOPSi$)

After LiPPh_2 had been added, as described in the synthesis of **4**, the solution was stirred for 3 h under exclusion of air. The protecting group was introduced by adding BH_3·*THF* (1 molar) in 6.58 cm^3 of *THF* to the solution and stirring for 3 h at room temperature. After removal of the solvent the residue was chromatographed (SiO_2, 35×4 cm) with petroleum ether:ethyl acetate = 6:1. The main fraction was **14** forming a colourless solid. Yield 2.80 g (76%); mp 87–89°C; PI FD MS (CH_2Cl_2): $m/z = 559$ (M, 8), 546 (M–BH_3, 6), 502 (M–$C(CH_3)_3$, 100); ^{1}H NMR (400 MHz, CD_3OD, *TMS*): $\delta =$ 7.63 (m, 9H, Ph, Py), 7.41 (m, 13H, Ph, Py), 7.06 (m, 1H, Py), 4.55 (s, CH_2OSi), 3.81 (d, $J = 12.0$ Hz, CH_2P), 1.09 (s, $C(CH_3)_3$) ppm; $^{31}P\{^{1}H\}$ NMR (CD_3OD, H_3PO_4 ext.): $\delta = 19.75$ (d, $J = 50.4$ Hz, PPh_2BH_3) ppm; IR (KBr): $\bar{\nu} = 2400$ (s) cm^{-1}.

Trihydroborane[6-(diphenylphosphanyl-κP-methyl)-2-(hydroxymethyl)pyridine] (**15**, $C_{19}H_{21}BNOP$)

Procedure as described for **14**, including molar amounts of reactants and quantities of solvent as in the synthesis of **5**. The eluent in the chromatography was petroleum ether:ethyl acetate = 1:2 to give **15** as a colourless solid. Yield 1.33 g (89%); mp 125–126°C; PI FD MS (CH_2Cl_2): $m/z = 321$ (M, 100), 307 (M–BH_3, 10); ^{1}H NMR (400 MHz, $CDCl_3$, *TMS*): $\delta = 7.70$ (m, 4H, Ph), 7.54 (ddd, $J = 7.7$, 7.7, 0.6 Hz, H^4-Py), 7.46 (m, 6H, Ph), 7.15 (ddd, $J = 7.7$, 1.8, 1.0 Hz, 1H, $H^{3/5}$-Py), 6.97 (ddd, $J = 7.7$, 1.8, 0.9 Hz, 1H, $H^{3/5}$-Py), 4.51 (d, $J = 4.8$ Hz, C$\underline{H}_2$OH), 3.84 (d, $J = 11.9$ Hz, CH_2P), 3.21 (t, $J = 4.8$ Hz, $CH_2O\underline{H}$) ppm; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = 18.78$ (d, $J = 65.6$ Hz, PPh_2BH_3) ppm; IR (KBr): $\nu = 2400$ (s) cm^{-1}.

Trihydroborane[6-(diphenylphosphanyl-κP-methyl)pyridine-2-carbaldehyde] (**16**, $C_{19}H_{19}BNOP$)

Procedure as described for **14**, including molar amounts of reactants and quantities of solvent as in the synthesis of **6**. The residue was chromatographed (SiO_2, 25×3 cm) with petroleum ether:ethyl acetate = 4:1. Compound **16** was obtained as a yellow solid. Yield 0.78 g (79%); mp 65–66°C; PI FD MS (CH_2Cl_2): $m/z = 319$ (M, 100), 305 (M–BH_3, 13); ^{1}H NMR (400 MHz, $CDCl_3$, *TMS*): $\delta = 9.75$ (s, CHO), 7.73 (m, 6H, Ph, Py), 7.45 (m, 7H, Ph, Py), 3.93 (d, $J = 12.0$ Hz, CH_2P) ppm; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = 18.97$ (d, $J = 68.7$ Hz, PPh_2BH_3) ppm; IR (KBr): $\bar{\nu} = 2380$ (s), 1710 (s) cm^{-1}.

Trihydroborane[6-(diphenylphosphanyl-κP-methyl)pyridine-2-carbaldoxime]
(**17**, $C_{19}H_{20}BN_2OP$)

Procedure as described for **14**, including molar amounts of reactants and quantities of solvent as in the synthesis of **7**. The residue was chromatographed (SiO_2, 25×3 cm) with petroleum ether:ethyl acetate = 1:1. Compound **17** was obtained as a colourless solid. Yield 6.22 g (99%); mp 139–140°C; PI FD MS (CH_2Cl_2): $m/z = 334$ (M, 45), 320 (M–BH_3, 100); ^{1}H NMR (400 MHz, *DMSO*-d_6, *TMS*): $\delta = 11.72$ (s, HCNO<u>H</u>), 7.77 (d, $J = 1.3$ Hz, <u>H</u>CNOH), 7.74 (m, 4H, Ph), 7.67 (dd, $J = 7.7$, 7.7 Hz, H^4-Py), 7.54 (m, 7H, Ph, H^5-Py), 7.15 (ddd, $J = 7.7$, 1.6, 1.3 Hz, H^3-Py), 4.05 (d, $J = 12.5$ Hz, CH_2P) ppm; ^{31}P{^{1}H} NMR (*DMSO*-d_6, H_3PO_4 ext.): $\delta = 18.65$ (bs, PPh_2BH_3) ppm; IR (KBr): $\bar{\nu} = 2380$ (s) cm^{-1}.

Trihydroborane[6-(diphenylphosphanyl-κP-methyl)pyridine-2-carbonitrile]
(**18**, $C_{19}H_{18}BN_2P$)

Procedure as described for **14**, including molar amounts of reactants and quantities of solvent as in the synthesis of **8**. Compound **18** formed a colourless solid. Yield 1.58 g (83%); mp 91°C; PI FD MS (CH_2Cl_2): $m/z = 316$ (M, 100), 302 (M–BH_3, 28); ^{1}H NMR (400 MHz, $CDCl_3$, *TMS*): $\delta = 7.70$ (m, 5H, Ph, Py), 7.57 (ddd, $J = 8.0$, 1.7, 1.1 Hz, H^5-Py), 7.48 (m, 7H, Ph, Py), 3.88 (d, $J = 12.1$ Hz, CH_2P) ppm; ^{31}P{^{1}H} NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = 18.82$ (d, $J = 65.2$ Hz, PPh_2BH_3) ppm; IR (KBr): $\bar{\nu} = 2400$ (s) cm^{-1}.

Trihydroborane[6-(diphenylphosphanyl-κP-methyl)pyridine-2-carbomethoxyimidate]
(**19**, $C_{20}H_{22}BN_2OP$)

Procedure as described for **14**, including molar amounts of reactants and quantities of solvent as in the synthesis of **9**. Compound **19** was obtained as a colourless solid. Purification by chromatography (Al_2O_3, 25×3 cm) with petroleum ether:ethyl acetate = 4:1 decreased the yield. Yield 1.15 g (82%); mp 88–89°C; PI FD MS (CH_2Cl_2): $m/z = 348$ (M, 76), 335 (M–BH_3, 100); ^{1}H NMR (250 MHz, $CDCl_3$, *TMS*): $\delta = 7.91$ (ddd, $J = 7.8$, 1.5, 1.1 Hz, H^3-Py), 7.74 (m, 4H, Ph), 7.68 (ddd, $J = 7.8$, 7.8, 0.5 Hz, H^4-Py), 7.44 (m, 7H, Ph, H^5-Py), 3.97 (d, $J = 12.1$ Hz, CH_2P), 3.93 (s, OCH_3) ppm; ^{31}P{^{1}H} NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = 18.79$ (d, $J = 66.7$ Hz, PPh_2BH_3) ppm; IR (KBr): $\bar{\nu} = 2390$ (s), 1720 (s) cm^{-1}.

General Procedure for the Synthesis of Compounds **20–23** *from* **19** *with 2-Aminoalcohols*

To a solution of 800 mg of **19** (2.30 mmol) in 40 cm^3 of CH_2Cl_2 a solution of 2.30 mmol of the corresponding 2-aminoalcohol (2.30 mmol) was added under N_2. Stirring was continued for 4 d at room temperature. After removal of the solvent the residue was chromatographed on Al_2O_3 (20×3 cm) with petroleum ether:ethyl acetate = 3:1.

(R)-Trihydroborane[2-(diphenylphosphanyl-κP-methyl)-6-(4-ethyl-4,5-dihydrooxazol-2-yl)pyridine] (**20**, $C_{23}H_{26}BN_2OP$)

From (*R*)-(−)-2-aminobutanol as aminoalcohol. Colourless resin. Yield 343 mg (38%); PI FD MS (CH_2Cl_2): $m/z = 388$ (M, 31), 374 (M–BH_3, 100); ^{1}H{^{31}P} NMR (400 MHz, $CDCl_3$, *TMS*): $\delta = 7.83$ (dd, $J = 7.7$, 1.0 Hz, H^3-Py), 7.73 (m, 4H, Ph), 7.60 (dd, $J = 7.7$, 7.8 Hz, H^4-Py), 7.44 (m, 7H, Ph, H^5-Py), 4.50 (dd, $J = 8.2$, 9.4 Hz, OC<u>H</u>^{A}H^{B}CHN), 4.27 (m, OCH^{A}H^{B}C<u>H</u>N), 4.09 (dd, $J = 8.2$, 8.2 Hz, OCH^A<u>H</u>^{B}CHN), 4.00 (d, $J = 14.0$ Hz, C<u>H</u>^{A}H^{B}PBH$_3$), 3.93 (d, $J = 14.0$ Hz, CH^A<u>H</u>^{B}PBH$_3$), 1.77 (m, C<u>H</u>^{A}H^{B}CH$_3$), 1.63 (m, CH^A<u>H</u>^{B}CH$_3$), 0.99 (t, $J = 7.3$ Hz, CH^{A}H^{B}C<u>H</u>$_3$) ppm; ^{31}P{^{1}H} NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = 18.56$ (d, $J = 48.8$ Hz, PPh_2BH_3) ppm; IR (KBr): $\bar{\nu} = 2390$ (s) cm^{-1}; $[\alpha]_D = +30.0$, $[\alpha]_{578} = +32.2$, $[\alpha]_{546} = +37.5$, $[\alpha]_{436} = +72.7$, $[\alpha]_{365} = +143.8°$ cm^3 g^{-1} dm^{-1} ($c = 2.67$, CH_2Cl_2).

(S)-Trihydroborane[2-(diphenylphosphanyl-κP-methyl)-6-(4-isopropyl-4,5-dihydrooxazol-2-yl)pyridine] (**21**, $C_{24}H_{28}BN_2OP$)

From (*S*)-(+)-valinol as aminoalcohol. Colourless resin. Yield 266 mg (30%); PI FD MS (CH_2Cl_2): $m/z = 402$ (M, 39), 388 (M–BH_3); $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$, *TMS*): $\delta = 7.85$ (dd, $J = 7.8$, 1.0 Hz, H^3-Py), 7.73 (m, 4H, Ph), 7.60 (dd, $J = 7.8$, 7.8 Hz, H^4-Py), 7.42 (m, 7H, Ph, H^5-Py), 4.44 (dd, $J = 9.0$, 7.6 Hz, $OC\underline{H}^A H^B CHN$), 4.15 (m, $OCH^A\underline{H}^B C\underline{H}N$), 4.02 (d, $J = 13.9$ Hz, $C\underline{H}^A H^B PBH_3$), 3.91 (d, $J = 13.9$ Hz, $CH^A\underline{H}^B PBH_3$), 1.89 (m, $C\underline{H}CH_3CH_3$), 1.03 (d, $J = 6.8$ Hz, $CHC\underline{H}_3CH_3$), 0.93 (d, $J = 6.8$ Hz, $CHCH_3C\underline{H}_3$) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = 18.62$ (d, $J = 48.8$ Hz, PPh_2BH_3) ppm; IR (KBr): $\bar{\nu} = 2390$ (s) cm^{-1}; $[\alpha]_D = -40.5$, $[\alpha]_{578} = -43.9$, $[\alpha]_{546} = -50.0$, $[\alpha]_{436} = -99.3$, $[\alpha]_{365} = -200.0°\ cm^3\ g^{-1}\ dm^{-1}$ ($c = 1.48$, CH_2Cl_2).

(S)-Trihydroborane[2-(diphenylphosphanyl-κP-methyl)-6-(4-benzyl-4,5-dihydrooxazol-2-yl)pyridine] (**22**, $C_{28}H_{28}BN_2OP$)

From (*S*)-(−)-phenylalaninol as aminoalcohol. Colourless resin. Yield 307 mg (30%); PI FD MS (CH_2Cl_2): $m/z = 450$ (M, 42), 436 (M–BH_3, 100); $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$, *TMS*): $\delta = 7.84$ (dd, $J = 7.8$, 1.1 Hz, H^3-Py), 7.74 (m, 4H, Ph), 7.61 (dd, $J = 7.8$, 7.8 Hz, H^4-Py), 7.42 (m, 7H, Ph, H^5-Py), 7.27 (m, 5H, Ph), 4.61 (m, $OCH^ACH^BC\underline{H}N$), 4.38 (dd, $J = 8.6$, 9.4 Hz, $OC\underline{H}^A H^B CHN$), 4.17 (dd, $J = 8.6$, 7.5 Hz, $OCH^A\underline{H}^B CHN$), 4.01 (d, $J = 13.8$ Hz, $C\underline{H}^A H^B PBH_3$), 3.93 (d, $J = 13.8$ Hz, $CH^A\underline{H}^B PBH_3$), 3.26 (dd, $J = 13.7$, 5.1 Hz, $C\underline{H}^A H^B PBH_3$), 2.74 (dd, $J = 13.7$, 8.9 Hz, $CH^A\underline{H}^B PBH_3$) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = 18.54$ (d, $J = 56.5$ Hz, PPh_2BH_3) ppm; IR (KBr): $\bar{\nu} = 2390$ (s) cm^{-1}; $[\alpha]_D = -29.9$, $[\alpha]_{578} = -29.9$, $[\alpha]_{546} = -34.0$, $[\alpha]_{436} = -68.7$, $[\alpha]_{365} = -134.7°\ cm^3\ g^{-1}\ dm^{-1}$ ($c = 1.47$, CH_2Cl_2).

(S)-Trihydroborane[2-(diphenylphosphanyl-κP-methyl)-6-(4-phenyl-4,5-dihydrooxazol-2-yl)pyridine] (**23**, $C_{27}H_{26}BN_2OP$)

From (*S*)-(−)-phenylglycinol as aminoalcohol. Colourless resin. Yield 378 mg (38%); PI FD MS (CH_2Cl_2): $m/z = 437$ (M, 34), 422 (M–BH_3, 100); $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$, *TMS*): $\delta = 7.96$ (dd, $J = 7.7$, 1.5 Hz, H^3-Py), 7.69 (m, 5H, Ph, H^4-Py), 7.38 (m, 12H, Ph, H^5-Py), 5.41 (dd, $J = 10.1$, 8.5 Hz, $OC\underline{H}^A H^B CHN$), 5.15 (m, $OCH^A H^B C\underline{H}N$), 4.83 (dd, $J = 10.1$, 8.6 Hz, $OCH^A\underline{H}^B CHN$), 4.03 (d, $J = 13.8$ Hz, $C\underline{H}^A H^B PBH_3$), 3.94 (d, $J = 13.8$ Hz, $CH^A\underline{H}^B PBH_3$) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = 18.73$ (d, $J = 47.3$ Hz, PPh_2BH_3) ppm; IR (KBr): $\bar{\nu} = 2400$ (s) cm^{-1}; $[\alpha]_D = +60.5$, $[\alpha]_{578} = +63.8$, $[\alpha]_{546} = +76.2$, $[\alpha]_{436} = +155.2$, $[\alpha]_{365} = +330.5°\ cm^3\ g^{-1}\ dm^{-1}$ ($c = 1.05$, CH_2Cl_2).

General Procedure for the Synthesis of the Borane-free Compounds **24**–**27** (*and* **32**)

In an atmosphere of dry N_2 0.75 mmol of the borane complex were dissolved in 15 cm^3 of Et_2NH and stirred for 5 h at 50°C. After removing the solvent and the volatiles, the residue was dried for 2 h in high vacuum with gentle heating to give the borane-free products **24**–**27** and **32**.

(R)-2-[(Diphenylphosphanyl)methyl]-6-(4-ethyl-4,5-dihydrooxazol-2-yl)pyridine (**24**, $C_{23}H_{23}N_2OP$)

From **20**. Colourless resin. Yield 261 mg (93%); PI DCI MS: $m/z = 391$ (M + NH_4, 100), 375 (MH, 8); $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$, *TMS*): $\delta = 7.84$ (dd, $J = 7.8$, 1.0 Hz, H^3-Py), 7.45 (m, 5H, Ph, H^4-Py), 7.31 (m, 6H, Ph), 6.96 (dd, $J = 7.8$, 1.0 Hz, H^5-Py), 4.55 (dd, $J = 8.2$, 9.5 Hz, $OC\underline{H}^A H^B CHN$), 4.28 (m, $OCH^A H^B C\underline{H}N$), 4.13 (dd, $J = 8.2$, 8.2 Hz, $OCH^A\underline{H}^B CHN$), 3.76 (d, $J = 13.5$ Hz, $C\underline{H}^A H^B PPh_2$), 3.72 (d, $J = 13.5$ Hz, $CH^A\underline{H}^B PPh_2$), 1.81 (m, $C\underline{H}^A H^B CH_3$), 1.63 (m, $CH^A\underline{H}^B CH_3$), 1.01 (t, $J = 7.4$ Hz,

$CH^AH^BC\underline{H}_3$) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = -10.17$ (s, PPh_2) ppm; $[\alpha]_D = +15.0$, $[\alpha]_{578} = +19.4$, $[\alpha]_{546} = +21.9$, $[\alpha]_{436} = +26.9^\circ\,cm^3\,g^{-1}\,dm^{-1}$ ($c = 2.12$, CH_2Cl_2).

(S)-2-[(Diphenylphosphanyl)methyl]-6-(4-isopropyl-4,5-dihydrooxazol-2-yl)pyridine
(**25**, $C_{24}H_{25}N_2OP$)

From **21**. Colourless resin. Yield 270 mg (93%); PI FD MS (CH_2Cl_2): $m/z = 388$ (M, 100); $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$, *TMS*): $\delta = 7.86$ (ddd, $J = 7.8$, 1.1, 1.1 Hz, H^3-Py), 7.50 (ddd, $J = 7.8$, 7.8, 0.3 Hz, H^4-Py), 7.44 (m, 4H, Ph), 7.31 (m, 6H, Ph), 6.97 (ddd, $J = 7.8$, 1.1, 1.2 Hz, H^5-Py), 4.49 (dd, $J = 8.2$, 9.5 Hz, $OC\underline{H}^AH^BCHN$), 4.22 (dd, $J = 8.2$, 8.3 Hz, $OCH^A\underline{H}^BCHN$), 4.14 (m, $OCH^AH^BC\underline{H}N$), 3.76 (d, $J = 13.3$ Hz, $C\underline{H}^AH^BPPh_2$), 3.71 (d, $J = 13.3$ Hz, $CH^A\underline{H}^BPPh_2$), 1.90 (m, $C\underline{H}CH_3CH_3$), 1.05 (d, $J = 6.8$ Hz, $CHC\underline{H}_3CH_3$), 0.94 (d, $J = 6.8$ Hz, $CHCH_3C\underline{H}_3$) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = -10.10$ (s, PPh_2) ppm; $[\alpha]_D = -16.6$, $[\alpha]_{578} = -17.9$, $[\alpha]_{546} = -21.2$, $[\alpha]_{436} = -41.3^\circ\,cm^3\,g^{-1}\,dm^{-1}$ ($c = 3.92$, CH_2Cl_2).

(S)-2-[(Diphenylphosphanyl)methyl]-6-(4-benzyl-4,5-dihydrooxazol-2-yl)pyridine
(**26**, $C_{28}H_{25}N_2OP$)

From **22**. Colourless resin. Yield 288 mg (88%); PI FD MS (CH_2Cl_2): $m/z = 436$ (M, 100); $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$, *TMS*): $\delta = 7.84$ (ddd, $J = 7.8$, 1.2, 1.1 Hz, H^3-Py), 7.52 (ddd, $J = 7.8$, 7.8, 0.3 Hz, H^4-Py), 7.44 (m, 4H, Ph), 7.31 (m, 8H, Ph), 7.25 (m, 3H, Ph), 6.98 (ddd, $J = 7.8$, 1.2, 1.2 Hz, H^5-Py), 4.63 (m, $OCH^AH^BC\underline{H}N$), 4.43 (dd, $J = 8.6$, 9.4 Hz, $OC\underline{H}^AH^BCHN$), 4.23 (dd, $J = 8.6$, 7.6 Hz, OCH^AH^BCHN), 3.76 (d, $J = 13.4$ Hz, $CH^AH^BPPh_2$), 3.72 (d, $J = 13.4$ Hz, $CH^A\underline{H}^BPPh_2$), 3.30 (dd, $J = 13.7$, 4.8 Hz, $C\underline{H}^AH^BPh$), 2.75 (dd, $J = 13.7$, 9.3 Hz, $CH^A\underline{H}^BPh$) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = -10.06$ (s, PPh_2) ppm; $[\alpha]_D = -15.3$, $[\alpha]_{578} = -17.4$, $[\alpha]_{546} = -20.4$, $[\alpha]_{436} = -47.0^\circ\,cm^3\,g^{-1}\,dm^{-1}$ ($c = 0.98$, CH_2Cl_2).

(S)-2-[(Diphenylphosphanyl)methyl]-6-(4-phenyl-4,5-dihydrooxazol-2-yl)pyridine
(**27**, $C_{27}H_{23}N_2OP$)

From **23**. Colourless resin. Yield 285 mg (90%); PI DCI MS: $m/z = 423$ (MH, 100), 239 (MH–PPh_2, 50); $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$, *TMS*): $\delta = 7.94$ (ddd, $J = 7.8$, 2.1, 1.1 Hz, H^3-Py), 7.53 (dd, $J = 7.8$, 7.8 Hz, H^4-Py), 7.36 (m, 15H, Ph), 7.01 (ddd, $J = 7.8$, 1.1, 1.2 Hz, H^5-Py), 5.42 (dd, $J = 8.5$, 10.3 Hz, $OCH^AH^BC\underline{H}N$), 4.88 (dd, $J = 8.5$, 10.3 Hz, $OC\underline{H}^AH^BCHN$), 4.37 (dd, $J = 8.5$, 8.5 Hz, $OCH^A\underline{H}^BCHN$), 3.78 (d, $J = 13.2$ Hz, $C\underline{H}^AH^BPPh_2$), 3.74 (d, $J = 13.2$ Hz, $CH^A\underline{H}^BPPh_2$) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = -9.83$ (s, PPh_2) ppm; $[\alpha]_D = +15.5$, $[\alpha]_{578} = +16.9$, $[\alpha]_{546} = +21.0$, $[\alpha]_{436} = +43.9^\circ\,cm^3\,g^{-1}\,dm^{-1}$ (c = 1.48, CH_2Cl_2).

Trihydroborane[(S)-N-Boc-4-(diphenylphosphanyl-κP-methyl)-2,2-dimethyloxazolidine]
(**29**, $C_{23}H_{33}BNO_3P$)

(*S*)-*N*-Boc-2,2-dimethyl-4-(tosyloxymethyl)oxazolidine (**28**, 1.50 g, 3.89 mmol) was dissolved in 50 cm^3 of *THF* under N_2. An equimolar amount of $LiPPh_2$ in *THF* was added dropwise at 0°C. After stirring for 3 h at 0°C 3.89 cm^3 of a solution of BH_3·*THF* (3.89 mmol) were added and the solution was stirred for 3 h at room temperature. The solvent was removed and the residue was chromatographed (SiO_2, 25 × 3 cm) with petroleum ether:ethyl acetate = 6:1. **29** was obtained as a colourless solid. Yield 1.10 g (68%); mp 82–83°C; PI FD MS (CH_2Cl_2): $m/z = 413$ (M, 7), 399 (M–BH_3, 100); ^1H NMR (250 MHz, $CDCl_3$, *TMS*): Two isomers, ratio 1:1.4; signals of the minor isomer in brackets: $\delta = 7.70$ (m, 10H, Ph), 4.29 [3.85] (m, $CH^A\underline{H}^BO$), 4.09 [3.66] (m, CHNBoc), 4.15 [3.78] (m, $C\underline{H}^AH^BO$), 3.09 [2.59] (m, $C\underline{H}^AH^BP$), 2.59 [2.29] (m, $CH^A\underline{H}^BP$), 1.51 (m, $C(CH_3)_2$) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = 11.74$ (m, PPh_2BH_3) ppm; IR (KBr): $\bar{\nu} = 2380$ (s) cm^{-1}.

Trihydroborane[(S)-2-amino-3-diphenylphosphanyl-κP-propanol]hydrochloride
(**30**, $C_{15}H_{21}BNOP{\cdot}HCl$)

Under N_2 200 mg of **29** (0.4 mmol) were dissolved in 5 cm^3 of *Me*OH. To this solution 5 cm^3 of a methanol solution saturated with HCl were added at 0°C. With a reaction time of 5 min it is possible to cleave the oxazolidine ring without destroying the phosphorus-borane complex. **30** was formed as the hydrochloride. Yield 124 mg (100%); PI DCI MS: $m/z = 274$ (MH, 4), 260 (M–BH_3, 100), 187 (Ph_2PH, 35); ^1H NMR (250 MHz, $CDCl_3$, *TMS*): $\delta = 8.15$ (bs, CHN$\underline{H}_3$Cl), 7.70 (m, 4H, H^2-Ph), 7.40 (m, 6H, H^3-Ph, H^4-Ph), 3.63 (m, HOC$\underline{H}_2$C$\underline{H}$NH_2), 2.86 (m, CH_2P) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = 12.43$ (s, PPh_2BH_3) ppm; IR (KBr): $\bar{\nu} = 2390$ (s) cm^{-1}.

Trihydroborane[(S)-2-[4-(diphenylphosphanyl-κP-methyl)-4,5-dihydrooxazol-2-yl]pyridine] (**31**, $C_{21}H_{22}BN_2OP$)

Pyridine-2-carbomethoxyimidate (375 mg, 1.21 mmol) was dissolved in 20 cm^3 of CH_2Cl_2 and 151 mm^3 of **30** (1.21 mmol) were added. After addition of 171 mm^3 of NEt_3 (2.3 mmol) to deprotect the amino function of **30**, the solution was stirred for 4 d at room temperature. The solvent was removed and the residue was chromatographed (Al_2O_3, 20 × 1.5 cm) with petroleum ether:ethyl acetate = 3:1. **31** was isolated as a colourless resin. Yield 388 mg (40%); PI FD MS (CH_2Cl_2): $m/z = 360$ (M, 89), 346 (M–BH_3, 100); $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$, *TMS*): $\delta = 8.70$ (ddd, $J = 4.8, 1.8, 0.9$ Hz, H^6-Py), 7.90 (ddd, $J = 7.9, 1.1, 0.9$ Hz, H^3-Py), 7.80 (m, 2H, Ph), 7.76 (ddd, $J = 7.6, 7.9, 1.8$ Hz, H^4-Py), 7.68 (m, 2H, Ph), 7.47 (m, 6H, Ph), 7.39 (ddd, $J = 4.8, 7.6, 1.1$ Hz, H^5-Py), 4.59 (dd, $J = 8.7, 17.7$ Hz, OC$\underline{H}^A$H^{B}CHN), 4.52 (m, OCH^{A}H^{B}C$\underline{H}$N), 4.28 (dd, $J = 8.7, 7.1$ Hz, OCH$^A\underline{H}^B$CHN), 3.16 (dd, $J = 14.4, 2.5$ Hz, C$\underline{H}^A$H^{B}P), 2.35 (dd, $J = 14.4, 10.6$ Hz, CH$^A\underline{H}^B$P) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = 12.28$ (d, $J = 62.6$ Hz, PPh_2BH_3) ppm; IR (KBr): $\bar{\nu} = 2380$ (s) cm^{-1}; $[\alpha]_D = +32.0$, $[\alpha]_{578} = +32.8$, $[\alpha]_{546} = +40.0$, $[\alpha]_{436} = +84.4$, $[\alpha]_{365} = +180.0°\ cm^3\ g^{-1}\ dm^{-1}$ (c = 1.25, CH_2Cl_2).

(S)-2-[4-[(Diphenylphosphanyl)methyl]-4,5-dihydrooxazol-2-yl]pyridine
(**32**, $C_{21}H_{19}N_2OP$)

From **31** according to the general procedure for removal of the BH_3 protecting group. Colourless resin. Yield 235 mg (90%); PI FD MS (CH_2Cl_2): $m/z = 346$ (M, 100); $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$, *TMS*): $\delta = 8.69$ (ddd, $J = 4.8, 1.8, 0.9$ Hz, H^6-Py), 7.96 (ddd, $J = 7.9, 1.1, 0.9$ Hz, H^3-Py), 7.74 (ddd, $J = 7.9, 7.6, 1.8$ Hz, H^4-Py), 7.51 (m, 2H, Ph), 7.43 (m, 2H, Ph), 7.37 (ddd, $J = 4.8, 7.6, 1.8$ Hz, H^5-Py), 7.33 (m, 6H, Ph), 4.53 (dd, $J = 8.4, 9.1$ Hz, OC$\underline{H}^A$H^{B}CHN), 4.37 (m, OCH^{A}H^{B}C$\underline{H}$N), 4.26 (dd, $J = 8.4, 7.9$ Hz, OCH$^A\underline{H}^B$CHN), 2.86 (ddd, $J = 13.5, 4.1, 1.9$ Hz, C$\underline{H}^A$H^{B}PPh_2), 2.22 (ddd, $J = 13.5, 10.2, 2.7$ Hz, CH$^A\underline{H}^B$PPh_2) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): $\delta = -22.03$ (s, PPh_2) ppm; $[\alpha]_D = +16.9$, $[\alpha]_{578} = +18.8$, $[\alpha]_{546} = +21.1$, $[\alpha]_{436} = +37.0°\ cm^3\ g^{-1}\ dm^{-1}$ (c = 3.84, CH_2Cl_2).

(S)-2-[4-[2-(Methylthio)ethyl]-4,5-dihydrooxazol-2-yl]pyridine
(**33**, $C_{11}H_{14}H_2OS$)

$[\alpha]_D = -88.2$, $[\alpha]_{578} = -94.1$, $[\alpha]_{546} = -107.8$, $[\alpha]_{436} = -201.0$, $[\alpha]_{365} = -371.6°\ cm^3\ g^{-1}\ dm^{-1}$ (c = 1.02, CH_2Cl_2).

(S)-2-[4-[2-(Methylthio)ethyl]-4,5-dihydrooxazol-2-yl]pyridine·$CuCl_2$
(**34**, $C_{11}H_{14}Cl_2CuN_2OS$)

To a solution of 87.4 mg of **33** (0.39 mmol) in 15 cm^3 of *Me*OH, a solution of 67.0 mg of $CuCl_2{\cdot}2H_2O$ (0.40 mmol) in 5 cm^3 of *Me*OH was added. The colour changed immediately to blue/turquoise. After stirring for 2 h at room temperature the solvent was removed. The residue was dissolved in a small

amount of *Me*OH and ether was added. After a few days at $-30°C$ green crystals were obtained, which were suitable for X-ray structure analysis. Yield 110 mg (77%); LT PI LSI MS: $m/z = 385$ (M + *Me*OH, 16), 320 (M–Cl, 73), 285 (M–2Cl, 100).

X-Ray Structure Analysis of **14** *and* **34**

Data were collected with an imaging plate diffraction system (Stoe-IPDS, Stoe & CIE GmbH, Darmstadt, Germany), using Mo-Kα radiation, $\lambda = 0.71073$ Å, with a graphite monochromator. Numerical absorption correction was applied for compound **34**. For data reduction the Stoe-IPDS software (Stoe 1998) was used [28]. The structure was solved with direct methods (SIR-97) [29] and refined by full-matrix least-squares techniques (SHELXL 97) [30]. All H atoms were included at calculated positions and refined using a riding model.

These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

Crystal data of **14**. $C_{35}H_{39}BNOPSi$, $M = 559.54$, $T = 173(1)$ K, translucent colourless prism, monoclinic, $P2_1/a$, $a = 14.8737(9)$, $b = 12.4055(6)$, $c = 18.1180(12)$ Å, $\beta = 112.640(7)°$, $V = 3085.4(4)$ Å^3, $Z = 4$, $\mu = 0.156$ mm^{-1}, reflections collected = 27171, independent = 5009, final R indices [$I > 2\sigma_I$]: $R_1 = 0.0412$, $wR_2 = 0.1101$. CCDC 199583.

Crystal data of **34**. $C_{11}H_{14}Cl_2CuN_2OS$, $M = 356.76$, $T = 173(1)$ K, translucent blue-green rod, orthorhombic, $P2_12_12_1$, $a = 8.3529(6)$, $b = 10.7267(7)$, $c = 16.0409(13)$ Å, $V = 1437.25(18)$ Å^3, $Z = 4$, $\mu = 2.025$ mm^{-1}, reflections collected = 18994, independent = 2741, final R indices [$I > 2\sigma_I$]: $R_1 = 0.0207$, $wR_2 = 0.0488$. CCDC 199582.

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