Self-Assembly of Bidentate Ligands for Combinatorial Homogeneous Catalysis

Asymmetric Rhodium-Catalyzed Hydrogenation

Bernhard Breit,* Martine Weis, Christoph Waloch and Wolfgang Seiche

Institut für Organische Chemie und Biochemie, Albert-Ludwigs-Universität Freiburg, Germany

Supplementary Material

(24 pages)

I	General	S-1
II	Experimental procedures and characterizations	S-3
	1 Preparation of aminopyridinyl phosphines	S-3
	2 Preparation of aminopyridinyl phosphonites	S-8
	3 Preparation of isoquinolinyl phosphonites	S-12
III	General procedure for asymmetric hydrogenation	S-16
IV	Heterodimeric platinum complexes	S-17
V	Heterodimeric cationic rhodium complexes	S-19
VI	Literature	S-24

I General

Bisdiethylamino-chloro-phosphine,^[1] 2-(trimethylsilyl)ethanol,^[2] the BINOL-derivatives,^[3] 2-amino-6-bromopyridine,^[4] 2-bromo-6-*N*-pivaloylaminopyridine^[5] and 1,3-dibromo-isoquinoline^[6] were synthesized according to literature procedures. The unsymmetrical disubstituted chlorophosphines can be prepared according to literature.^[7] Methyl-2-acetamidoacrylate and dimethylitaconate were purchased from Aldrich and Jansen Chimica, methyl- α -acetylamino cinnamate^[8] was synthesized according to literature procedures.

All reactions were carried out in dried glassware under an argon atmosphere 5.0 (Südwest-Gas). Air and moisture sensitive liquids and solutions were transferred via syringe. All reagents were obtained commercially unless otherwise noted. All solvents were dried and distilled by standard procedures. Organic solutions were concentrated under reduced pressure by rotary evaporation. Chromatographic purification of products was accomplished using flash chromatography^[9] on a Merck silica gel Si 60[®] (200-400 mesh).

Nuclear magnetic resonance spectra were acquired on a Varian Mercury spectrometer (300 MHz, 121 MHz and 75 MHz for ^1H , ^{31}P and ^{13}C respectively), on a Bruker AMX 400 (400 MHz, 162 MHz and 100 MHz for ^1H , ^{31}P and ^{13}C respectively) and on a Bruker DRX 500 (500 MHz, 202 MHz and 125 MHz for ^1H , ^{31}P and ^{13}C respectively) and are referenced according to residual protio solvent signals. Data for ^1H -NMR are recorded as follows: chemical shift (δ in ppm), multiplicity (s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet; p, pseudo), coupling constant (Hz), integration. Data for ^{13}C -NMR are reported in terms of chemical shift (δ in ppm), multiplicity (if not a singlet), coupling constant (Hz).

High-resolution mass spectra were obtained on a Finnigan MAT 8200 instrument and ESI mass spectrometry was performed on a Finnigan *LCQ Advantage*. Elementary analysis was performed on an elemental vario (Fa. Elementar Analysensysteme GmbH). Optical rotations were measured on a Perkin-Elmer 241 polarimeter.

Separation of the enantiomers was achieved on a Chiralpak AD-H column using a Knauer K-2501 UV-detector. The enantiomeric excess of the triarylphosphine ligands was determined by HPLC using a Chiralpak AD-H column.

Hydrogenation experiments were performed following the general procedure using hydrogen gas 5.0 (Südwest-Gas).

II Experimental procedures and characterizations

I Preparation of aminopyridinyl phosphines

(*rac*)-6-(*o*-Anisylphenylphosphino)-2-pivaloylaminopyridine (**4a**)

To a solution of 2.42 g 2-bromo-6-*N*-pivaloylaminopyridine (9.4 mmol, 0.8 eq.) in 30 ml THF was added at -100°C 11.7 ml *n*-butyl-lithium (1.60 M in hexane, 18.8 mmol, 1.6 eq.) during 20 min. The mixture was stirred for 1 h, then a solution of 2.95 g *o*-anisylchlorophosphine (11.8 mmol, 1.0 eq.) in 10 ml THF was added slowly. After stirring 30 min at -100°C , the yellow solution was allowed to warm to room temperature and stirred 24 h at this temperature. The solvent was removed under reduced pressure and the residue was filtrated through a plug of silica to remove salts. The filtrate was concentrated in vacuo and purified via flash chromatography (Cy:EtOAc 10:1) to yield 1.84 g of the title compound **4a** (4.7 mmol, 50%) as a white foam.

$^1\text{H-NMR}$ (400 MHz, C_6D_6): δ 8.51 (d, $J = 8.2$ Hz, 1H), 7.88 (br s, 1H), 7.52-7.48 (m, 2H), 7.12-7.05 (m, 5H), 7.04-7.00 (m, 1H), 6.82 (d, $J = 7.3$ Hz, 1H), 6.74 (dd, $J = 7.3, 7.3$ Hz, 1H), 6.50 (dd, $J = 8.2, 4.7$ Hz, 1H), 3.19 (s, 3H), 0.86 (s, 9H); **$^{13}\text{C-NMR}$** (100 MHz, C_6D_6): δ 176.5, 162.7 (d, $J_{\text{C,P}} = 4.3$ Hz), 161.9 (d, $J_{\text{C,P}} = 14.5$ Hz), 152.6 (d, $J_{\text{C,P}} = 14.5$ Hz), 137.9, 136.7 (d, $J_{\text{C,P}} = 11.6$ Hz), 135.1 (d, $J_{\text{C,P}} = 20.3$ Hz), 134.3 (d, $J_{\text{C,P}} = 2.9$ Hz), 130.6, 139.1, 128.8 (d, $J_{\text{C,P}} = 7.3$ Hz), 128.0 (d, $J_{\text{C,P}} = 21.8$ Hz), 126.0 (d, $J_{\text{C,P}} = 14.5$ Hz), 123.8 (d, $J_{\text{C,P}} = 11.6$ Hz), 112.5, 110.7, 55.2, 39.5, 27.0; **$^{31}\text{P-NMR}$** (121 MHz, C_6D_6): δ -14.2 ; **CHN**: calcd. C: 70.39, H: 6.42, N: 7.14 found C: 70.16, H: 6.62, N: 6.97.

The enantiomers of **4a** were separated via preparative chiral HPLC (Chiralpak AD-H, *n*-heptane:*i*-PrOH 100:5, rt, 12.0 ml/min, 295 nm); (–)-enantiomer : 6.4 min, $[\alpha]_{\text{D}}^{21} = -22.8$ ($c = 0.98$, CHCl_3); (+)-enantiomer: 11.9 min, $[\alpha]_{\text{D}}^{21} = +22.6$ ($c = 1.01$, CHCl_3).

(The analytical and spectroscopic data of the enantiomers correspond to the racemate)

(rac)-6-(1-Naphthylphenylphosphino)-2-pivaloylaminopyridine (4b)

$C_{26}H_{25}N_2OP$

Mol. Wt.: 412.46

To a solution of 1.80 g 2-bromo-6-*N*-pivaloylaminopyridine (7.0 mmol, 1.0 eq.) in 30 ml THF was added at $-100^{\circ}C$ 8.7 ml *n*-butyl-lithium (1.60 M in hexane, 14.0 mmol, 2.0 eq.) during 20 min. The mixture was stirred for 1 h, then a solution of 1.89 g 1-naphthylphenylchlorophosphine (7.0 mmol, 1.0 eq.) in 10 ml THF was slowly added. After stirring 30 min at $-100^{\circ}C$, the yellow solution was allowed to warm to room temperature and stirred 12 h at this temperature. After addition of 30 ml sat. aqueous $NaHCO_3$ solution, the aqueous layer was extracted with EtOAc (3×20 ml), the combined organic layers were dried ($MgSO_4$) and concentrated. The crude product was purified via flash chromatography (Cy:EtOAc 10:1) to yield 1.50 g of the title compound **4b** (3.6 mmol, 52%) as a white foam.

1H -NMR (500 MHz, C_6D_6): δ 8.77-8.75 (m, 1H), 8.51 (d, $J = 7.5$ Hz, 1H), 7.92 (br s, 1H), 7.60-7.57 (m, 2H), 7.47-7.43 (m, 2H), 7.29 (td, $J = 5.6, 1.1$ Hz, 1H), 7.19-7.17 (m, 2H), 7.11 (t, $J = 7.7$ Hz, 1H), 7.05-7.04 (m, 3H), 6.93 (td, $J = 7.6, 1.9$ Hz, 1H), 6.66 (d, $J = 7.5$ Hz, 1H), 0.86 (s, 9H); **^{13}C -NMR** (125 MHz, C_6D_6): δ 176.5, 161.9 (d, $J_{C,P} = 6.4$ Hz), 152.8 (d, $J_{C,P} = 15.1$ Hz), 138.2 (d, $J_{C,P} = 1.5$ Hz), 136.3 (d, $J_{C,P} = 22.1$ Hz), 136.0 (d, $J_{C,P} = 10.9$ Hz), 135.1 (d, $J_{C,P} = 20.6$ Hz), 134.4 ($J_{C,P} = 15.1$ Hz), 134.0 (d, $J_{C,P} = 4.2$ Hz), 132.9 (d, $J_{C,P} = 1.2$ Hz), 130.0, 129.3, 129.0, 128.9 (d, $J_{C,P} = 7.3$ Hz), 126.7 (d, $J_{C,P} = 18.1$ Hz), 126.6, 126.4 (d, $J_{C,P} = 1.5$ Hz), 126.0 (d, $J_{C,P} = 1.8$ Hz), 124.5 (d, $J_{C,P} = 11.8$ Hz), 112.8, 39.5, 27.1; **^{31}P -NMR** (162 MHz, C_6D_6): δ -12.6; **CHN**: calcd. C: 75.71, H: 6.11, N: 6.79 found C: 75.45, H: 5.97, N: 6.57.

The enantiomers of **4b** were separated via preparative chiral HPLC (Chiralpak AD-H, *n*-heptane:EtOH 70:3, rt, 11.0 ml/min, 295 nm); (–)-enantiomer : 5.7 min, $[\alpha]_D^{20} = -9.4$ ($c = 1.00$, $CHCl_3$); (+)-enantiomer: 11.9 min, $[\alpha]_D^{20} = +10.1$ ($c = 1.01$, $CHCl_3$).

(The analytical and spectroscopic data of the enantiomers correspond to the racemate)

6-Brom-2-*N*-trifluororacetylaminopyridine

$C_7H_4BrF_3N_2O$

Mol. Wt.: 269.02

To a solution of 7.3 ml trifluoroacetic acid anhydride (10.92 g, 52.0 mmol, 3.0 eq.) in 40 ml CH_2Cl_2 was added slowly at 0°C 7.2 ml triethylamine (5.26 g, 52.0 mmol, 3.0 eq.). After 5 min 3.00 g 2-amino-6-bromopyridine (17.3 mmol, 1.0 eq.) was added and the solution was stirred at room temperature for 3 days. The conversion was monitored via TLC. After addition of 30 ml sat. aqueous $NaHCO_3$ solution, the aqueous layer was extracted with EtOAc (4 × 30 ml), the combined organic layers were dried ($MgSO_4$) and concentrated. The crude product was purified via flash chromatography (Cy:EtOAc 5:1) to yield 3.96 g of the title compound (14.7 mmol, 85%) as a yellow oil.

1H -NMR (500 MHz, $CDCl_3$): δ 8.61 (br s, 1H), 8.15 (d, J = 8.2 Hz, 1H), 7.66 (pt, J = 8.0 Hz, 1H), 7.36 (d, J = 7.7 Hz, 1H); **^{13}C -NMR** (125 MHz, $CDCl_3$): δ 155.0 (q, $J_{C,F}$ = 38.8 Hz), 148.9, 141.1, 139.9, 125.9, 115.4 (q, $J_{C,F}$ = 288.6 Hz), 111.9; **CHN**: calcd. C: 31.25, H: 1.50, N: 10.41 found C: 31.40, H: 1.20, N: 10.36.

(rac)-6-(*o*-Tolylphenylphosphino)-2-aminopyridine

C₁₈H₁₇N₂P

Mol. Wt.: 292.31

To a solution of 1.88 g 6-bromo-2-*N*-trifluoroacetylaminopyridine (7.0 mmol, 0.95 eq.) in 40 ml THF was added at –100°C 8.8 ml *n*-butyl-lithium (1.60 M in hexane, 14.0 mmol, 1.90 eq.) during 20 min. The mixture was stirred for 90 min, then a solution of 1.73 g *o*-tolylphenylchlorophosphine (7.4 mmol, 1.0 eq.) in 10 ml THF was slowly added. After stirring 30 min at –100°C, the yellow solution was allowed to warm to room temperature and stirred 12 h at this temperature. The solvent was removed under reduced pressure and the residue was filtrated through a plug of silica to remove salts. The filtrate was concentrated in vacuo and purified via flash chromatography (Cy:EtOAc 10:1) to furnish 1.12 g of the protected title compound (4.7 mmol, 41%) as a white foam.

500 mg (1.29 mmol) were directly deprotected by stirring in 10 ml MeOH with 1.78 g K₂CO₃ (12.29 mmol) at 60°C for 4 h. After addition of 5 ml sat. aqueous NaHCO₃ solution, the aqueous layer was extracted with EtOAc (4 × 20 ml), the combined organic layers were dried (MgSO₄) and concentrated. The crude product was purified via flash chromatography (Cy:EtOAc 1:1) to yield 0.33 g of the title compound (1.14 mmol, 88%) as a white solid.

¹H-NMR (400 MHz, CDCl₃): δ 7.26-7.23 (m, 5H), 7.20-7.11 (m, 3H), 7.01 (pt, *J* = 7.2 Hz, 1H), 6.78-6.75 (m, 1H), 6.26 (d, *J* = 8.3 Hz, 1H), 6.21 (d, *J* = 7.3 Hz, 1H), 4.50 (br s, 2H), 2.35 (s, 3H); **¹³C-NMR** (100 MHz, CDCl₃): δ 159.9 (d, *J*_{C,P} = 9.2 Hz), 157.5 (d, *J*_{C,P} = 16.4 Hz), 141.7 (d, *J*_{C,P} = 25.4 Hz), 136.3 (d, *J*_{C,P} = 1.5 Hz), 134.5 (d, *J*_{C,P} = 10.6 Hz), 134.3 (d, *J*_{C,P} = 12.3 Hz), 133.4 (d, *J*_{C,P} = 19.8 Hz), 132.1, 129.0 (d, *J*_{C,P} = 4.8 Hz), 127.9, 127.8, 127.5 (d, *J*_{C,P} = 7.3 Hz), 125.0 (d, *J*_{C,P} = 1.0 Hz), 117.6 (d, *J*_{C,P} = 11.1 Hz), 106.8, 20.2 (d, *J*_{C,P} = 21.3 Hz); **³¹P-NMR** (121 MHz, CDCl₃): δ –12.1; **CHN**: calcd. C: 73.96, H: 5.86, N: 9.58 found C: 73.65, H: 5.87, N: 9.50.

The enantiomers were separated via preparative chiral HPLC (Chiralpak AD-H, *n*-heptane:EtOH 95:5, rt, 11.0 ml/min, 282 nm); (–)-enantiomer : 6.8 min, [α]_D²¹ = –17.3 (c = 1.00, CHCl₃); (+)-enantiomer: 8.5 min, [α]_D²¹ = +17.1 (c = 1.0, CHCl₃).

(The analytical and spectroscopic data of the enantiomers correspond to the racemate)

(+)-6-(*o*-Tolylphenylphosphino)-2-pivaloylaminopyridine ((+)-4c)

$C_{23}H_{25}N_2OP$

Mol. Wt.: 376.43

To a solution of 94 mg (+)-6-(*o*-tolylphenylphosphino)-2-aminopyridine (0.32 mmol, 1.0 eq.) in 25 ml CH_2Cl_2 was added consecutively at 0°C 85 μ l triethylamine (62 mg, 0.61 mmol, 1.9 eq.) and 59 μ l pivaloylchloride (58 mg, 0.48 mmol, 1.5 eq.). After warming to room temperature the solution was stirred for 36 h. The solvent was removed in vacuo and the residue was purified via flash chromatography (Cy:EtOAc 5:1) to yield 108 mg of the title compound (0.29 mmol, 89%) as a white foam.

1H -NMR (500 MHz, C_6D_6): δ 8.52 (d, J = 8.5 Hz, 1H), 7.89 (br s, 1H) 7.44-7.41 (m, 2H), 7.10-6.99 (m, 7H), 6.94 (dd J = 7.4, 7.4 Hz, 1H), 6.70 (d, J = 7.7 Hz, 1H), 2.44 (s, 3H), 0.85 (s, 9H); **^{13}C -NMR** (125 MHz, C_6D_6): δ 176.5, 162.0 (d, $J_{C,P}$ = 5.5 Hz), 152.8 (d, $J_{C,P}$ = 14.8 Hz), 143.1 (d, $J_{C,P}$ = 26.0 Hz), 138.2 (d, $J_{C,P}$ = 1.2 Hz), 136.1 (d, $J_{C,P}$ = 11.5 Hz), 135.8 (d, $J_{C,P}$ = 12.7 Hz), 134.9 (d, $J_{C,P}$ = 20.6 Hz), 133.7, 130.5 (d, $J_{C,P}$ = 4.9 Hz), 129.2 (d, $J_{C,P}$ = 3.0 Hz), 129.0 (d, $J_{C,P}$ = 7.3 Hz), 126.6, 124.0 (d, $J_{C,P}$ = 11.5 Hz), 112.8, 39.5, 27.0, 21.3 (d, $J_{C,P}$ = 11.8 Hz); **^{31}P -NMR** (121 MHz, C_6D_6): δ -11.7; **HRMS**: calcd. 376.1704 found 376.1693; **$[\alpha]_D^{20}$** = +4.0 (c = 1.00, $CHCl_3$).

The enantiomer (–)-**4c** was synthesized as described above starting from (–)-6-(*o*-tolylphenylphosphino)-2-aminopyridine.

(The analytical and spectroscopic data correspond to the (+)-enantiomer)

$[\alpha]_D^{20}$ = –3.9 (c = 1.05, $CHCl_3$).

6-(Bisdiethylaminophosphino)-2-pivaloylaminopyridine

Mol. Wt.: 352.45

To a solution of 2-bromo-6-*N*-pivaloylaminopyridine (7.7 mmol, 1.0 eq.) in 75 ml THF was added slowly at -100°C 10.0 ml *n*-butyl-lithium (1.54 M in hexane, 15.4 mmol, 2.0 eq.). The mixture was stirred for 90 min at -100°C , then 1.62 g bisdiethylamino-chloro-phosphine (7.7 mmol, 1.0 eq.) was added in one portion. The solution was allowed to warm to room temperature overnight. The solvent was removed under reduced pressure, then 40 ml Et_2O and 140 μl degassed water (140 mg, 7.7 mmol, 1.0 eq.) were added successively and the resulting suspension was filtered over Celite[®] and MgSO_4 under an argon atmosphere. After removal of the solvent in vacuo, the crude product was purified by bulb-to-bulb distillation ($60^{\circ}\text{C}/1\cdot 10^{-3}$ mbar to remove impurity, $205^{\circ}\text{C}/1\cdot 10^{-3}$ mbar) to yield 1.41 g of the title compound (4.0 mmol, 52%) as a yellow oil.

^1H -NMR (300 MHz, C_6D_6): δ 8.48 (dd, $J = 5.0, 4.0$ Hz, 1H), 8.01 (br s, 1H), 7.25 (d, $J = 3.1$ Hz, 2H), 3.07 (m, 8H), 1.10 (t, $J = 7.0$ Hz, 12H), 1.05 (s, 9H); **^{13}C -NMR** (100 MHz, C_6D_6): δ 176.1, 164.8 (d, $J_{\text{C,P}} = 13.1$ Hz), 152.4 (d, $J_{\text{C,P}} = 7.3$ Hz), 137.6, 122.8 (d, $J_{\text{C,P}} = 21.8$ Hz), 111.6 (d, $J_{\text{C,P}} = 2.9$ Hz), 43.9 (d, $J_{\text{C,P}} = 17.4$ Hz), 39.6, 27.3, 14.9 (d, $J_{\text{C,P}} = 2.9$ Hz); **^{31}P -NMR** (121 MHz, C_6D_6): δ 94.3; **CHN calcd.** C: 61.34, H: 9.44, N: 15.90 found C: 61.30, H: 9.21, N: 15.57.

General procedure: Synthesis of aminopyridinyl phosphonites

6-(Bisdiethylaminophosphino)-2-pivaloylaminopyridine (0.2-0.6 mmol) was dissolved in toluene (44 ml/mmol) and the enantiomerically pure BINOL-derivative (1.0 eq.) was added. The mixture was heated to 96°C in a closed Schlenk tube. Diethylamine formed during the reaction was removed several times under vacuum. Conversion was monitored by ^{31}P -NMR. The solvent was removed under reduced pressure and the residue taken up in pentane twice to give the title compound as a yellowish foam in quantitative yield.

Analytical data for (*S*)-5a:

$\text{C}_{30}\text{H}_{25}\text{N}_2\text{O}_3\text{P}$
Mol. Wt.: 492.50

^1H -NMR (300 MHz, C_6D_6): δ 8.56 (d, J = 8.5 Hz, 1H), 8.10 (br s, 1H), 7.65 (d, J = 8.6 Hz, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.55-7.42 (m, 4H), 7.30 (d, J = 8.7 Hz, 1H), 7.13-6.93 (m, 5H), 6.88 (d, J = 7.2 Hz, 1H), 6.77 (dd, J = 8.1, 7.6 Hz, 1H), 0.99 (s, 9H); ^{13}C -NMR (100 MHz, C_6D_6): δ 175.2, 159.5 (d, $J_{\text{C,P}}$ = 20.8 Hz), 152.2, 151.4 (d, $J_{\text{C,P}}$ = 16.2 Hz), 148.7 (d, $J_{\text{C,P}}$ = 2.9 Hz), 148.2 (d, $J_{\text{C,P}}$ = 6.5 Hz), 136.6, 133.1, 132.8 (d, $J_{\text{C,P}}$ = 1.2 Hz), 132.2 (d, $J_{\text{C,P}}$ = 1.4 Hz), 129.9, 129.5, 128.4 (d, $J_{\text{C,P}}$ = 15.0 Hz), 127.4, 127.3, 125.9 (d, $J_{\text{C,P}}$ = 9.2 Hz), 125.3 (d, $J_{\text{C,P}}$ = 13.8 Hz), 124.3, 124.0, 122.9 (d, $J_{\text{C,P}}$ = 2.9 Hz), 122.4, 120.3 (d, $J_{\text{C,P}}$ = 1.2 Hz), 119.4 (d, $J_{\text{C,P}}$ = 9.9 Hz), 117.2, 114.3, 111.8, 38.3, 25.8; ^{31}P -NMR (121 MHz, C_6D_6): δ 167.6; HRMS: calcd. 491.1535 found 491.1525; $[\alpha]_{\text{D}}^{21}$ = -30.0 (c = 0.57, CHCl_3).

Analytical data for (S)-5b:

$\text{C}_{32}\text{H}_{29}\text{N}_2\text{O}_3\text{P}$
Mol. Wt.: 520.56

^1H -NMR (400 MHz, C_6D_6): δ 8.55 (d, $J = 8.3$ Hz, 1H), 8.04 (br s, 1H), 7.67 (d, $J = 8.2$ Hz, 1H), 7.58 (dd, $J = 9.4, 8.2$ Hz, 2H), 7.55 (s, 1H), 7.45 (d, $J = 8.5$ Hz, 1H), 7.31 (s, 1H), 7.22-7.18 (m, 2H), 7.00-6.93 (m, 2H), 6.84 (dd, $J = 7.3, 0.8$ Hz, 1H), 6.74 (dd, $J = 8.0, 7.7$ Hz, 1H), 2.49 (s, 3H), 1.87 (s, 3H), 0.98 (s, 9H); **^{13}C -NMR** (100 MHz, C_6D_6): δ 176.5, 161.0 (d, $J_{\text{C,P}} = 20.8$ Hz), 152.6 (d, $J_{\text{C,P}} = 17.4$ Hz), 149.0 (d, $J_{\text{C,P}} = 3.4$ Hz), 148.6 (d, $J_{\text{C,P}} = 6.8$ Hz), 138.0, 132.5 (d, $J_{\text{C,P}} = 1.7$ Hz), 132.2, 131.6, 130.9, 130.5, 130.1 (d, $J_{\text{C,P}} = 1.5$ Hz), 129.7 (d, $J_{\text{C,P}} = 1.0$ Hz), 127.4, 127.2, 125.8, 125.7, 125.7, 125.5 (d, $J_{\text{C,P}} = 6.0$ Hz), 125.3, 125.2, 124.3 (d, $J_{\text{C,P}} = 2.9$ Hz), 120.7 (d, $J_{\text{C,P}} = 10.4$ Hz), 115.9, 39.6, 27.1, 17.2 (d, $J_{\text{C,P}} = 1.9$ Hz), 16.9; **^{31}P -NMR** (121 MHz, C_6D_6): δ 163.4; **HRMS**: calcd. 520.1908 found 520.1916; $[\alpha]_{\text{D}}^{21} = +22.5$ (c = 0.44, CHCl_3).

Analytical data for (S)-5c:

$C_{44}H_{37}N_2O_3P$

Mol. Wt.: 672.75

1H -NMR (400 MHz, C_6D_6): δ 8.35 (ddd, $J = 8.1, 1.5, 1.3$ Hz, 1H), 7.98 (s, 1H), 7.76 (d, $J = 8.1$ Hz, 1H), 7.68 (s, 1H), 7.69-7.66 (m, 4H), 7.59 (d, $J = 8.3$ Hz, 1H), 7.47 (br s, 1H), 7.25 (ddd, $J = 7.6, 1.3, 1.0$ Hz, 1H), 7.20 (ddd, $J = 7.3, 1.5, 1.0$ Hz, 1H), 7.05 (m, 2H), 6.99 (m, 4H), 6.88 (d, $J = 8.1$ Hz, 2H), 6.70 (dd, $J = 7.3, 1.5$ Hz, 1H), 6.67 (dd, $J = 8.1, 7.3$ Hz, 1H), 2.14 (s, 3H), 2.05 (s, 3H), 1.00 (s, 9H); **^{13}C -NMR** (100 MHz, C_6D_6): δ 175.9, 159.5 (d, $J_{C,P} = 19.3$ Hz), 152.0 (d, $J_{C,P} = 17.4$ Hz), 147.5 (d, $J_{C,P} = 2.9$ Hz), 146.9 (d, $J_{C,P} = 5.8$ Hz), 137.0 (d, $J_{C,P} = 20.3$ Hz), 135.9, 135.6, 135.1 (d, $J_{C,P} = 1.9$ Hz), 135.0, 134.8, 133.0 (d, $J_{C,P} = 1.9$ Hz), 132.5, 131.9, 131.4, 131.2, 130.0 (d, $J_{C,P} = 1.9$ Hz), 129.8, 129.5, 129.0, 128.6, 128.5, 128.4, 127.1, 127.1, 126.4, 126.3, 126.3, 125.4, 125.3, 120.1 (d, $J_{C,P} = 10.6$ Hz), 115.7, 39.3, 27.1, 21.2, 20.9; **^{31}P -NMR** (121 MHz, C_6D_6): δ 164.9; **HRMS**: calcd. 672.2521 found 672.2542; $[\alpha]_D^{20} = +33.8$ (c = 0.76, $CHCl_3$).

3-Bromo-1-(2-(trimethylsilyl)ethoxy)isoquinoline

To a suspension of 2.60 g potassium-*tert*-butylate (23.1 mmol, 1.2 eq.) in 80 ml THF was added at 0°C 2.50 g 2-(trimethylsilyl)ethanol (21.2 mmol, 1.1 eq.) and the mixture was stirred at this temperature for 30 min. Then a solution of 5.53 g 1,3-dibromoisquinoline (19.3 mmol, 1.0 eq.) in 30 ml THF was added slowly and the resulting suspension was stirred at room temperature for another 90 min. The reaction mixture was quenched by addition of 100 ml sat. aqueous NH_4Cl solution, the aqueous layer was extracted with EtOAc (3×100 ml) and the combined organic layers were dried (MgSO_4) and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (Cy:EtOAc 95:5) to yield 6.00 g of the title compound (18.5 mmol, 96%) as a colorless liquid.

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 8.19 (d, $J = 8.3$ Hz, 1H), 7.65-7.60 (m, 2H), 7.51 (ddd, $J = 7.4, 7.2, 1.9$ Hz, 1H), 7.40 (s, 1H), 4.63 (m, 2H), 1.24 (m, 2H), 0.13 (s, 9H); **$^{13}\text{C-NMR}$** (125 MHz, CDCl_3): δ 160.2, 139.5, 132.5, 131.2, 126.7, 125.3, 124.6, 118.6, 116.9, 65.3, 17.5, -1.2, **CHN** calcd. C: 51.85, H: 5.59, N: 4.32 found C: 51.71, H: 5.55, N: 4.26.

3-(Bisdiethylaminophosphino)isoquinolin-1(2H)-one

$C_{17}H_{26}N_3OP$

Mol. Wt.: 319.38

To a solution of 2.00 g 3-bromo-1-(2-(trimethylsilyl)-ethoxy)isoquinoline (6.2 mmol, 1.0 eq.) in 35 ml THF was added slowly at -100°C 4.7 ml *n*-butyl-lithium (1.3 M in hexane, 6.2 mmol, 1.0 eq.). The mixture was stirred for 20 min at this temperature, then 1.30 g bisdiethylamino-chloro-phosphine (6.2 mmol, 1.0 eq.) was added in one portion. The solution was allowed to warm to room temperature and stirring was continued for another 20 min. The reaction mixture was quenched by addition of 200 μl degassed water and then concentrated in vacuo. The residue was transferred to a separating funnel with degassed water and CH_2Cl_2 . The aqueous layer was separated and extracted with CH_2Cl_2 (2×50 ml). The combined organic layers were dried (MgSO_4) and concentrated under reduced pressure to yield 2.58 g of crude protected 3-(bis(diethylamino)phosphino)isoquinoline (6.15 mmol, quant.) as a yellow oil, which was immediately deprotected in the next step.

To a solution of 1.45 g protected 3-(bis(diethylamino)phosphino)isoquinoline (3.5 mmol, 1.0 eq.) in 15 ml THF was added 3.8 ml TBAF (1 M in THF, 3.8 mmol, 1.1 eq.) and the mixture was stirred at room temperature for 3 h. The reaction was quenched by addition of 15 ml degassed water and 50 ml Et_2O . The organic layer was separated and washed with degassed water (4×15 ml) and dried (MgSO_4). The crude solid was washed with $\text{Et}_2\text{O}:\text{PE}$ (30-50) 1:4 several times to yield 0.60 g of the title compound (1.9 mmol, 54%) as a cream coloured solid.

$^1\text{H-NMR}$ (300 MHz, C_6D_6): δ 8.91 (br s, 1H), 8.78 (d, $J = 7.9$ Hz, 1H), 7.27-7.11 (m, 3H), 6.50 (s, 1H), 2.92-2.80 (m, 8H), 0.91 (pt, $J = 7.0$ Hz, 12H); **$^{13}\text{C-NMR}$** (100 MHz, C_6D_6): δ 162.9, 142.1 (d, $J_{\text{C,P}} = 4.4$ Hz), 138.5 (d, $J_{\text{C,P}} = 2.9$ Hz), 132.4, 128.2, 127.9, 126.7, 126.2, 109.1 (d, $J_{\text{C,P}} = 16.0$ Hz), 43.4 (d, $J_{\text{C,P}} = 17.4$ Hz), 14.6 (d, $J_{\text{C,P}} = 4.4$ Hz); **$^{31}\text{P-NMR}$** (121 MHz, C_6D_6): δ 87.8; **HRMS**: calcd. 319.1816 found 319.1814.

(S)-and (R)-6a:

To a solution of 0.11 g 3-(bisdiethylaminophosphino)isoquinolin-1(2*H*)-one (0.34 mmol, 1.0 eq.) in 12 ml toluene was added 0.10 g binaphthol (0.35 mmol, 1.0 eq.). The mixture was heated at reflux under a stream of dry argon until the volume of solvent had been reduced to 1 ml. Toluene was added and the mixture heated to reflux for several hours. Conversion was monitored by ^{31}P -NMR. The solvent was removed under reduced pressure, the residue purified by adding 10 ml Et_2O and filtering off the insolubles. The filtrate was concentrated in vacuo to yield 0.13 g of the title compound **6a** (0.27 mmol, 80%) as a cream coloured solid.

^1H -NMR (400 MHz, C_6D_6): δ 8.90 (br s, 1H), 8.65 (d, $J = 8.0$ Hz, 1H), 7.64 (dd, $J = 8.8, 8.1$ Hz, 2H), 7.49 (d, $J = 8.1$ Hz, 1H), 7.40 (m, 3H), 7.34 (d, $J = 8.9$ Hz, 1H), 7.05-6.89 (m, 7H), 6.84 (ddd, $J = 7.7, 1.0$ Hz, 1H), 6.62 (d, $J = 10.1$ Hz, 1H); **^{13}C -NMR** (100 MHz, C_6D_6): δ 161.3, 153.5, 149.2 (d, $J_{\text{C,P}} = 10.2$ Hz), 149.2 (d, $J_{\text{C,P}} = 2.0$ Hz), 140.3 (d, $J_{\text{C,P}} = 52.1$ Hz), 136.5 (d, $J_{\text{C,P}} = 11.8$ Hz), 134.3, 133.4 (d, $J_{\text{C,P}} = 1.7$ Hz), 132.7 (d, $J_{\text{C,P}} = 1.0$ Hz), 132.5, 132.2 (d, $J_{\text{C,P}} = 1.0$ Hz), 131.3, 131.2 (d, $J_{\text{C,P}} = 6.5$ Hz), 127.6, 127.3, 127.1, 127.0, 126.9, 125.5 (d, $J_{\text{C,P}} = 10.9$ Hz), 124.8, 124.0, 123.3 (d, $J_{\text{C,P}} = 2.7$ Hz), 121.3 (d, $J_{\text{C,P}} = 1.5$ Hz), 121.0, 118.3, 114.3 (d, $J_{\text{C,P}} = 42.0$ Hz), 112.0; **^{31}P -NMR** (121 MHz, C_6D_6): δ 162.2; **HRMS**: calcd. 459.1023 found 459.1024; (*S*)-**6a**: $[\alpha]_{\text{D}}^{21} = +95.3$ ($c = 0.60$, CHCl_3); (*R*)-**6a**: $[\alpha]_{\text{D}}^{20} = -104.1$ ($c = 0.66$, CHCl_3).

(S)-6b:

$C_{31}H_{22}NO_3P$

Mol. Wt.: 487.49

To a solution of 0.22 g 3-(bis(diethylamino)phosphino)isoquinolin-1(2*H*)-one (0.69 mmol, 1.00 eq.) in 6 ml *m*-xylene was added 0.16 g (*S*)-3,3'-dimethyl-2,2'-dihydroxy-1,1'-binaphthyl (0.52 mmol, 0.75 eq.). The mixture was heated at reflux under a stream of dry argon until the volume of solvent had been reduced to 1 ml. Again *m*-xylene was added and the mixture heated to reflux for another 3-6 h. Conversion was monitored by ^{31}P -NMR. The solvent was removed under reduced pressure, the residue purified by adding 15 ml Et₂O and filtering off the insolubles. The filtrate was concentrated in vacuo to furnish 0.24 g of the title compound (*S*)-**6b** (0.48 mmol, 92%) as a white solid.

1H -NMR (400 MHz, C₆D₆): δ 8.51 (d, J = 7.8 Hz, 1H), 8.27 (br s, 1H), 7.67 (d, J = 8.2 Hz, 1H), 7.59 (d, J = 8.2 Hz, 1H), 7.55 (s, 1H), 7.43 (pt, J = 8.1 Hz, 2H), 7.36 (s, 1H), 7.22 (d, J = 7.2 Hz, 1H), 7.13-6.85 (m, 6H), 6.62 (d, J = 12.0 Hz, 1H), 2.44 (s, 3H), 1.96 (s, 3H); ^{13}C -NMR (100 MHz, C₆D₆): δ 160.4, 152.4, 148.3 (d, $J_{C,P}$ = 5.8 Hz), 148.0 (d, $J_{C,P}$ = 2.9 Hz), 140.5 (d, $J_{C,P}$ = 52.2 Hz), 136.1 (d, $J_{C,P}$ = 13.5 Hz), 132.7, 132.2, 132.1 (d, $J_{C,P}$ = 1.9 Hz), 132.0 (d, $J_{C,P}$ = 0.7 Hz), 131.5, 130.9, 130.7, 130.7, 129.8, 129.6 (d, $J_{C,P}$ = 1.9 Hz), 128.5, 127.1, 127.0, 126.9 (d, $J_{C,P}$ = 1.9 Hz), 126.5, 125.9 (d, $J_{C,P}$ = 12.1 Hz), 125.4 (d, $J_{C,P}$ = 2.9 Hz), 124.3, 123.9, 114.6 (d, $J_{C,P}$ = 46.4 Hz), 111.0, 16.9, 16.7; ^{31}P -NMR (121 MHz, C₆D₆): δ 156.5; HRMS: calcd. 487.1320 found 487.1337; $[\alpha]_D^{21}$ = -175.7 (c = 0.51, CHCl₃).

III General procedure for asymmetric hydrogenation

2.0 mg $[\text{Rh}(\text{COD})_2]\text{BF}_4$ ($5.0 \cdot 10^{-3}$ mmol, 1.0 mol%), L_1 ($5.5\text{-}6.5 \cdot 10^{-3}$ mmol, 1.1-1.3 mol%) and L_2 ($5.5\text{-}6.5 \cdot 10^{-3}$ mmol, 1.1-1.3 mol%) were dissolved in 5 ml of solvent and stirred at room temperature for 30 min. Subsequently the appropriate substrate (0.5 mmol, 1 eq.) was added in one portion.

For hydrogenation at atmospheric pressure, the reaction vessel was evacuated and refilled with hydrogen gas four times. Following this procedure, the yellow reaction mixture was vigorously stirred under an atmosphere of hydrogen (hydrogen balloon) at the indicated temperature.

For hydrogenations performed at higher pressure, the reaction mixture was transferred into a steel autoclave via syringe under an argon atmosphere. The reaction mixture was saturated with hydrogen gas by applying four cycles of careful evacuation and refilling with hydrogen gas followed by adjustment of the reaction pressure indicated.

Conversion was determined by ^1H -NMR after 24 h.

Hydrogenation of acetamidoacrylate:

Enantiomeric excess was determined by chiral GC analysis using a Hydrodex- β -TBDAc column, 25 m $\times$ 0.25 mm, 120°C

t_{R} [(*R*)-enantiomer] = 14.0 min.

t_{R} [(*S*)-enantiomer] = 20.3 min.

Hydrogenation of methyl- α -acetylamino cinnamate 7:

Enantiomeric excess was determined by chiral HPLC analysis using a Chiralpak-AD column, 25 cm $\times$ 4.6 mm, *n*-heptane:*i*-propanol 90:10, 254 nm

t_{R} [(*R*)-enantiomer] = 15.0 min.

t_{R} [(*S*)-enantiomer] = 19.5 min.

Hydrogenation of dimethylitaconate 8:

Enantiomeric excess was determined by chiral GC analysis using a G-TA, Trifluoroacetyl- γ -Cyclodextrin column, 30 m $\times$ 0.5 mm, 75°C

t_{R} [(*S*)-enantiomer] = 32.2 min.

t_{R} [(*R*)-enantiomer] = 35.2 min.

IV Heterodimeric platinum complexes

Platinum complex of (*R*)-**6a** and 6-DPPAP:

To a solution of 14.5 mg [*cis*-PtCl₂(1,5-COD)] ($4.01 \cdot 10^{-2}$ mmol, 1.0 eq.) in 0.4 ml CDCl₃ was added a solution of 18.4 mg isoquinolone (*R*)-**6a** ($4.01 \cdot 10^{-2}$ mmol, 1.0 eq.) and 14.5 mg aminopyridinyl-derivative 6-DPPAP ($4.01 \cdot 10^{-2}$ mmol, 1.0 eq.) in 0.4 ml CDCl₃. The formation of the heterodimeric complex [*cis*-PtCl₂(**6a**)(6-DPPAP)] was monitored by ³¹P-NMR.

³¹P-NMR (121 MHz, CDCl₃, 293 K): δ 107.5 (dd, $J_{\text{P,Pt}} = 4994.9$, $J_{\text{P,P}} = 15.0$ Hz), 13.9 (br d, $J_{\text{P,Pt}} = 3555.1$ Hz) ($J_{\text{P,P}}$ -coupling not resolved due to broad line width).

Platinum complex of (*R*)-**6a** and (–)-**4a**:

To a solution of 9.1 mg [*cis*-PtCl₂(1,5-COD)] ($2.43 \cdot 10^{-2}$ mmol, 1.0 eq.) in 0.4 ml CDCl₃ was added a solution of 11.2 mg isoquinolone (*R*)-**6a** ($2.43 \cdot 10^{-2}$ mmol, 1.0 eq.) and 10.0 mg aminopyridinyl-derivative (–)-**4a** ($2.43 \cdot 10^{-2}$ mmol, 1.0 eq.) in 0.4 ml CDCl₃. The formation of the heterodimeric complex [*cis*-PtCl₂(**6a**)(**4a**)] was monitored by ³¹P-NMR.

³¹P-NMR (202 MHz, CDCl₃, 320 K): δ 106.4 (dd, $J_{\text{P,Pt}} = 5020.8$, $J_{\text{P,P}} = 12.3$ Hz), 12.6 (br d, $J_{\text{P,Pt}} = 3617.9$ Hz) ($J_{\text{P,P}}$ -coupling not resolved due to broad line width).

V Heterodimeric cationic rhodium complexes

Rhodium complex of (*S*)-**5a** and 3-DPICon:

To a solution of 10.9 mg $[\text{Rh}(1,5\text{-COD})_2]\text{BF}_4$ ($2.68 \cdot 10^{-2}$ mmol, 1.0 eq.) in 0.4 ml CDCl_3 was added a solution of 8.8 mg 3-DPICon ($2.67 \cdot 10^{-2}$ mmol, 1.0 eq.) and 13.2 mg aminopyridinyl-derivative (*S*)-**5a** ($2.68 \cdot 10^{-2}$ mmol, 1.0 eq.) in 0.4 ml CDCl_3 . The formation of the heterodimeric complex $[\text{Rh}(1,5\text{-COD})(\mathbf{5a})(6\text{-DPICon})]$ was monitored by ^{31}P -NMR and mass spectrometry.

^{31}P -NMR (162 MHz, CDCl_3 , 293 K): δ 162.8 (dd, $J_{\text{P,Rh}} = 218.0$ Hz, $J_{\text{P,P}} = 35.7$ Hz), 154.7 (d, $J_{\text{P,Rh}} = 216.0$ Hz), 33.9 (br d, $J_{\text{P,Rh}} = 150.6$ Hz) ($J_{\text{P,P}}$ -coupling not resolved due to broad line width).

MS (ESI; $\text{C}_{59}\text{H}_{53}\text{BF}_4\text{N}_3\text{O}_4\text{P}_2\text{Rh}$, $M = 1119.26$ g/mol): $m/z = 622$ (27), 703 (48), 884 (11), 924 ($M^+ - \text{COD} - \text{BF}_4^-$, 100), 1087 (32).

Rhodium complex of (*S*)-**5a** and (*S*)-**6a**:

Mass spectrometry (ESI) proved the formation of the heterodimeric complex ($M^+ - BF_4^- = 1162$ (24), $M^+ - COD - BF_4^- = 1054$ (100)). However the ^{31}P -NMR showed a broad signal at a chemical shift of $\delta = 157$ ppm which confirms phosphonite ligand coordinated to a rhodium(I) center.^[10] The broad line width, which is a consequence of an unresolved dynamic process, did in this case not allow an unambiguous structural assignment. However, replacing COD by addition of the bidentate ligand 1,10-phenanthroline gave the defined complex $[Rh(\mathbf{5a})(\mathbf{6a})phen]BF_4$ described below. The ^{31}P -NMR of $[Rh(\mathbf{5a})(\mathbf{6a})phen]BF_4$ at 270K shows two ABX spin systems in accord with two diastereomeric heterodimer rhodium complexes in a ratio of 1.5:1.

The formation of diastereomers may result either from a distorted square planar coordination geometry at rhodium^[11] or alternatively, may be due to additional axial chirality as a consequence of a distortion in the hydrogen bond system of the ligand backbone (compare X-ray structure of a square planar platinum(II) complex of the parent heterodimer ligand system 6-DPPAP/3-DPICo published in ref. [5] in the communication).

Rhodium complex of (*S*)-**5a** and (*S*)-**6a** in the presence of 1,10-phenanthroline:

To a solution of 10.9 mg $[Rh(1,5-COD)_2]BF_4$ ($2.68 \cdot 10^{-2}$ mmol, 1.0 eq.) in 0.4 ml $CDCl_3$ was added a solution of 13.2 mg aminopyridinyl-derivative (*S*)-**5a** ($2.68 \cdot 10^{-2}$ mmol, 1.0 eq.) and 12.3 mg isoquinolone (*S*)-**6a** ($2.68 \cdot 10^{-2}$ mmol, 1.0 eq.) in 0.4 ml $CDCl_3$. After dissolution of the complex, 4.8 mg 1,10-phenanthroline ($2.66 \cdot 10^{-2}$ mmol, 1.0 eq.) was added causing the solution to turn red immediately. The formation of the heterodimeric complex $[Rh(\mathbf{5a})(\mathbf{6a})phen]BF_4$ was monitored by ^{31}P -NMR and mass spectrometry.

^{31}P -NMR (202 MHz, $CDCl_3$, 270 K): δ 181.0 (dd, $J_{P,Rh} = 235.6$ Hz, $J_{P,P} = 85.8$ Hz), 178.4 (d, $J_{P,Rh} = 246.1$ Hz), 177.9 (dd, $J_{P,Rh} = 241.2$ Hz, $J_{P,P} = 92.3$ Hz), 165.1 (dd, $J_{P,Rh} = 240.4$ Hz, $J_{P,P} = 85.9$ Hz), 164.4 (dd, $J_{P,Rh} = 229.6$ Hz, $J_{P,P} = 92.3$ Hz).

MS (ESI; $C_{71}H_{51}BF_4N_5O_6P_2Rh$, $M = 1321.24$ g/mol): $m/z = 1201$ (5), 1236 ($M^+ - BF_4^-$, 100), 1027 (35), 1307 (5).

$^1J_{P,Rh} = 235.6 \text{ Hz}$

$^1J_{P,Rh} = 241.2 \text{ Hz}$

$^2J_{P,P} = 85.8 \text{ Hz}$

$^2J_{P,P} = 92.3 \text{ Hz}$

taken at 270K

$^1J_{P,Rh} = 240.4 \text{ Hz}$ $^1J_{P,Rh} = 229.6 \text{ Hz}$

$^2J_{P,P} = 85.9 \text{ Hz}$ $^2J_{P,P} = 92.4 \text{ Hz}$

Rhodium complex of (*S*)-**5b** and (*S*)-**6a** in the presence of 1,10-phenanthroline:

Mass spectrometry (ESI) and ^{31}P -NMR prove the formation of the heterodimeric complex. In agreement with the spectrum shown above, two diastereomeric heterodimer rhodium complexes in a ratio of 1.5:1 were observed which result again from a distorted square planar geometry or supplementary axial chirality in the hydrogen bonded ligand backbone.

To a solution of 10.9 mg $[\text{Rh}(1,5\text{-COD})_2]\text{BF}_4$ ($2.68 \cdot 10^{-2}$ mmol, 1.0 eq.) in 0.4 ml CDCl_3 was added a solution of 14.0 mg aminopyridinyl-derivative (*S*)-**5b** ($2.69 \cdot 10^{-2}$ mmol, 1.0 eq.) and 12.3 mg isoquinolone (*S*)-**6a** ($2.68 \cdot 10^{-2}$ mmol, 1.0 eq.) in 0.4 ml CDCl_3 . After dissolution of the complex, 4.8 mg 1,10-phenanthroline ($2.66 \cdot 10^{-2}$ mmol, 1.0 eq.) was added causing the solution to turn red immediately. The formation of the heterodimeric complex $[\text{Rh}(\mathbf{5b})(\mathbf{6a})\text{phen}]\text{BF}_4$ was monitored by ^{31}P -NMR and mass spectrometry.

^{31}P -NMR (162 MHz, CDCl_3 , 270 K): δ 180.5 (dd, $J_{\text{P,Rh}} = 235.5$ Hz, $J_{\text{P,P}} = 86.7$ Hz), 180.2 (dd, $J_{\text{P,Rh}} = 242.7$ Hz, $J_{\text{P,P}} = 91.3$ Hz), 165.3 (dd, $J_{\text{P,Rh}} = 242.5$ Hz, $J_{\text{P,P}} = 87.0$ Hz), 159.5 (dd, $J_{\text{P,Rh}} = 227.5$ Hz, $J_{\text{P,P}} = 89.3$ Hz).

MS (ESI; $\text{C}_{73}\text{H}_{55}\text{BF}_4\text{N}_5\text{O}_6\text{P}_2\text{Rh}$, $M = 1349.27$ g/mol): $m/z = 1082$ ($\text{M}^+ - \text{phen} - \text{BF}_4^-$, 100), 1143 (78), 1262 ($\text{M}^+ - \text{BF}_4^-$, 59).

VI Literature

- [1] Sakai, J.; Schweizer, W.B.; Seebach, D. *Helv. Chim. Acta.* **1993**, 76, 2654-2665.
- [2] Davis, D. D.; Jacocks, H. M. *J. Organomet. Chem.* **1981**, 206, 33-47.
- [3] Simonsen, K. B.; Gothelf, K. V.; Jørgensen *J. Org. Chem.* **1998**, 63, 7536-7538 and references cited therein.
- [4] Den Hertog, H. J, Wibaut, J. P. *Recl. Trav. Chim. Pays* **1932**, 51, 381-387 and *ibid.* **1936**, 55, 122-125.
- [5] Mase, T. et al. *J. Org. Chem.* **2001**, 66, 6775-6786.
- [6] Osborn, A. R.; Schofield, K.; Short, L. N. *J. Chem. Soc.* **1956**, 4191-4206.
- [7] (a) Wittig, G.; Braun, H.; Cristau H. J. *Justus Liebigs Ann. Chem.* **1971**, 751, 17-26.
(b) Chodkiewicz, W.; Guillerme, D.; Jore, D.; Mathieu, E.; Wodzki, W. *J. Organomet. Chem.* **1984**, 269, 107-114.
- [8] Gladiali, S.; Pinna L. *Tetrahedron Asym.* **1991**, 2, 623-632.
- [9] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, 43, 2923-2925.
- [10] Van der Vlugt, J. I., Paulusse J. M. J., Zijp E. J., Tijmensen J. A., Mills A. M., Spek A. L., Claver C., Vogt D. *Eur. J. Inorg. Chem.* **2004**, 4193-4201.
- [11] (a) Jones R. A. et al. *J. Chem. Soc. Dalton Trans.* **1979**, 489-490. $[\text{Rh}(\text{PMe}_3)_4]^+$ has a tetrahedral coordinative geometry.
(b) Caldaran H., DeArmond, M. K., Hanck K. W., Sahini, V. E. *J. Am. Chem. Soc.* **1976**, 98, 4455-57. $[\text{Rh}(\text{phen})_2]^+$ has a distorted square planar structure.