



Supporting Information

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Catalysis by design: Wide bite angle diphosphines by assembly of ditopic ligands for selective rhodium catalyzed hydroformylation**

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General Procedures.

All manipulations were performed under argon using standard Schlenk-techniques, except the synthesis of N-(2-aminophenyl)-4-methylbenzenesulfonamide and 1-(1-ethoxyethoxy)-4-methylbenzene. All the solvent were obtained from Sigma-Aldrich and dried with an SPS of IT-Inc. All reagents were purchased from common commercial sources and used as received. All NMR spectra were obtained on a Bruker ATM-400 spectrometer. The spectra were recorded at the following frequencies: 400.13 MHz (^1H), 100.63 MHz ($^{13}\text{C}\{^1\text{H}\}$), and 161.98 MHz ($^{31}\text{P}\{^1\text{H}\}$). $^{13}\text{C}\{^1\text{H}\}$ - and $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra were recorded using broad band proton decoupling. Proton spectra are referenced to internal $\text{Si}(\text{CH}_3)_4$ (0 ppm) or residual CHCl_3 (7.27 ppm). $^{13}\text{C}\{^1\text{H}\}$ spectra are referenced to CDCl_3 (77.0 ppm). $^{31}\text{P}\{^1\text{H}\}$ spectra are referenced to 85% H_3PO_4 as external standard. Mass spectra were recorded using a Waters LCT Premier spectrometer. High resolution mass spectra were obtained on a Bruker Autoflex MALDI-TOF Mass Spectrometer.

X-ray structure determination was carried out on a Bruker-Nonius diffractometer equipped with an APPEX 2 4 K CCD area detector, a FR 591 rotating anode with Mo- $\text{K}\alpha$ radiation, Montel mirrors as monochromator, and a Kryoflex low temperature device ($T = -173\text{ }^\circ\text{C}$). Full-sphere data collection was used with ω and ϕ scans.

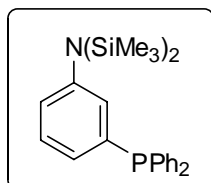
Hydroformylation experiments were performed in a semiautomated autoclave (AMTEC-Slurry Phase Reactor-SPR16) equipped with sixteen stainless steel 15 mL reactors and automated sampling under reaction conditions. All reactors were connected via a valve system with gas and liquid supply and equipped with individually adjustable stirring (magnetic stirring bars – 500 to 2000 rpm) and heating (external electrical heating jacket – up to $220\text{ }^\circ\text{C}$)

Gas chromatography analyses were performed on an Agilent Technologies 6890N/G1530N apparatus equipped with a FID detector, and a HP-5 column (length 30 m, internal diameter 0.32 mm, film thickness 0.25 μm).



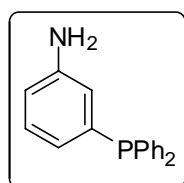
IR spectra were recorded on a FT IR Nicolet 5700 Thermo spectrometer.

Diphenyl{[N,N-bis(trimethylsilyl)amino]phenyl}phosphine



To a solution of 3-[N,N-bis(trimethylsilyl)amino]phenylmagnesium chloride (1M in THF, 25 mL, 25 mmol), chlorodiphenylphosphine (4.7 mL, 25.0 mmol) dissolved in THF (20 mL) was added at room temperature. After 2 hours of stirring, all volatiles were removed in vacuo. The residue was extracted with diethyl ether (80 mL). After removal of the solvents, the crude product was purified by short path distillation in vacuo (7.1 g, 16.8 mmol, 67%). ^1H NMR (CDCl_3): δ = 0.1 (s, 18H, CH_3), 6.4-7.1 (m, 14H, arom); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ = -2.8; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ = 135.4 (d, J_{CP} = 10.8 Hz), 135.1 (d, J_{CP} = 11.3 Hz), 133.2 (d, J_{CP} = 15.4 Hz), 131.6 (d, J_{CP} = 19.5 Hz), 128.4, 128.1, 127.1 (d, J_{CP} = 22.1 Hz), 126.5, 126.4, 126.3, 2.1 (SiMe_3).

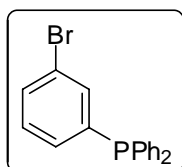
3-Diphenylphosphino aniline:



Diphenyl{[N,N-bis(trimethylsilyl)amino]phenyl}phosphine (7.1 g, 16.8 mmol), was dissolved in methanol (50 mL), and heated at reflux for 8-15 hours. The pure product precipitated from the reaction mixture as a colorless microcrystalline solid. It was isolated by filtration, and dried in vacuo (3.7 g, 13.3 mmol, 79 %). ^1H NMR (CDCl_3): δ = 4.1 (s, br, 2 H), 6.6-6.8 (m, 3 H), 7.14 (td, 1 H); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ = -4.7; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ = 146.4 (d, J_{CP} = 8.0 Hz), 138.1 (d, J_{CP} = 10.2 Hz), 137.3 (d, J_{CP} = 10.2 Hz), 133.8 (d, J_{CP} = 19.7 Hz), 129.4 (d, J_{CP} = 8.0 Hz), 128.6, 128.4 (d, J_{CP} =

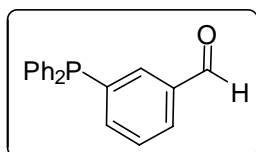
6.58 Hz), 124.5 (d, $J_{\text{CP}} = 20.5$ Hz), 120.0 (d, $J_{\text{CP}} = 20.5$ Hz), 115.5; MS (ESI): $m/z = 278.09$ ($M + H^+$).

(3-Bromophenyl)diphenylphosphine:



To a solution of 1,3-dibromobenzene (5.0 g, 20.5 mmol) in dry THF (40 mL) *n*-butyllithium (2.5 M in hexane, 8.5 mL, 21.2 mmol) was added dropwise under Ar, at -78 °C. The reaction mixture was stirred for 45 min. Chlorodiphenylphosphine (3.9 mL, 20.5 mmol) was added dropwise, and the reaction mixture was allowed to warm to room temperature. After 2 hours of stirring, the reaction mixture was quenched with water, and extracted with diethylether. The combined organic phase was dried over MgSO_4 . The solvents were evaporated in vacuo. The crude product was purified by distillation in vacuo. Colorless, viscous oil (4.8 g, 14.1 mmol, 67%). ^1H NMR (CDCl_3): $\delta = 7.5\text{--}7.1$ (m, 14H); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = -1.7$; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 140.5$ (d, $J_{\text{CP}} = 15.4$ Hz), 136.3 (d, $J_{\text{CP}} = 10.9$ Hz), 135.9 (d, $J_{\text{CP}} = 19.8$ Hz), 133.8 (d, $J_{\text{CP}} = 19.7$ Hz), 132.1 (d, $J_{\text{CP}} = 19.0$ Hz), 131.7, 130.0 (d, $J_{\text{CP}} = 6.5$ Hz), 129.1, 128.7 (d, $J_{\text{CP}} = 7.3$ Hz), 123.0 (d, $J_{\text{CP}} = 6.5$ Hz); MS (ESI): $m/z = 341.0$ ($M + H^+$).

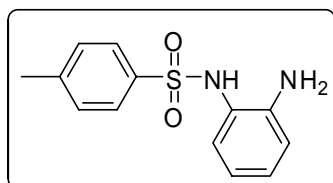
3-(diphenylphosphino)benzaldehyde:



To a solution of (3-bromophenyl)diphenylphosphine (15.1 g, 44.4 mmol) in anhydrous THF (250 mL) *n*-butyllithium (2.5M, 21.3 mL, 53.3mmol) was added dropwise under argon, at -78 °C. The orange solution was stirred at -78 °C for 30 min, and then dry DMF (6.8 mL, 88.4 mmol) was added. The mixture was allowed to warm up to room temperature and stirred for 30 min. The reaction mixture was quenched with water (20 mL) and extracted with ethyl acetate. The combined organic phase was washed with water and brine, and dried over MgSO_4 . The crude product was purified by column chromatography (hexane/ CH_2Cl_2 , 1:1). The product is a viscous yellow oil (7.9 g, 27.2

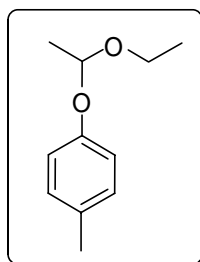
mmol, 78%). ^1H NMR (CDCl_3): δ = 9.9 (s 1H, CHO), 7.9 (dd, 1H, J_{HH} = 8.8 Hz, J_{HH} = 1.4 Hz, arom), 7.8 (dd, 1H, J_{HP} = 7.1 Hz, J_{HH} = 1.4 Hz, J_{HH} = 0.50 Hz, arom), 7.6-7.5 (m, 2H), 7.4-7.3 (m, 10H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ = -2.6; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ = 192.1, 139.4 (d, J_{CP} = 14.6 Hz), 139.3 (d, J_{CP} = 18.3 Hz), 136.4 (d, J_{CP} = 5.8 Hz), 136.2 (d, J_{CP} = 10.2 Hz), 135.2 (d, J_{CP} = 20.4 Hz), 133.8 (d, J_{CP} = 19.7 Hz), 129.3, 129.2, 129.1, 128.7 (d, J_{CP} = 7.3 Hz); MS (ESI): m/z = 291.1 ($\text{M} + \text{H}^+$).

N-(2-aminophenyl)-4-methylbenzenesulfonamide:



p-Toluenesulfonyl chloride (10.0 g, 51.4 mmol) in THF (50 mL) was added dropwise over a period of 12 hours to a solution of *o*-phenylenediamine (17.0 g, 154.2 mmol) and pyridine (4.9 g, 61.7 mmol) in THF (100 mL) at room temperature. When the reaction was complete (NMR), the solvent was evaporated in vacuo. Water (50 mL) was added to the dark oily residue, then it was extracted with CH_2Cl_2 . The organic phase was washed with brine, and dried over MgSO_4 . The solvent was removed in vacuo, and the crude product was purified by crystallization (ethanol/water). Colorless solid (11.9 g 45.4 mmol, 88%). Mp. 138 °C. ^1H NMR (CDCl_3): δ = 7.5 (d, 2H, J_{HH} = 8.9 Hz, arom), 7.9 (d, 2H, J_{HH} = 8.9 Hz, arom), 7.0 (ddd, 1H, J_{HH} = 7.9 Hz, J_{HH} = 1.7 Hz, J_{HH} = 0.75 Hz, arom), 6.7 (dd, 1H, J_{HH} = 7.9 Hz, J_{HH} = 1.5 Hz, arom), 6.5 (td, 1H, J_{HH} = 7.9 Hz, J_{HH} = 1.5 Hz, arom), 6.4 (dd, 1H, J_{HH} = 7.9 Hz, J_{HH} = 1.7 Hz, arom), 6.1 (bs, 1H, NH), 4.1 (bs, 1H, NH_2), 2.4 (s, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ = 144.5, 143.9, 135.9, 129.6, 128.9, 128.6, 127.6, 121.1, 118.5, 117.1, 21.6. MS (ESI): m/z = 263.0 ($\text{M} + \text{H}^+$).

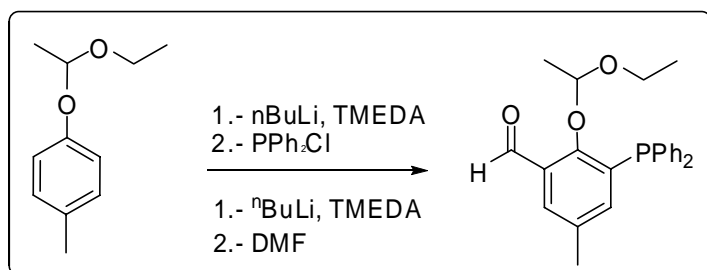
1-(1-ethoxyethoxy)-4-methylbenzene:



Trifluoroacetic acid (0.72 mL, 9.46 mmol) was added to a solution of *p*-cresol (10.3 g, 94.7 mmol), ethyl vinyl ether (27.4 mL, 284 mmol) and pyridine (2.3 mL, 28.4 mmol).

The reaction mixture was stirred for 48 hours at room temperature. When the reaction was complete, the excess of ethyl vinyl ether was evaporated in vacuo without heating. The resulting dark, non-viscous oil was dissolved in diethyl ether (60 mL). The organic solution was washed with NaOH solution (1M, 4 x 30 mL), water (30 mL) and brine (30 mL), then dried over MgSO₄. The diethyl ether was evaporated in vacuo. The crude product was purified by distillation (bp 60 °C, 1.9x10⁻¹ mbar). Colorless liquid (14.1 g, 78.2 mmol, 82%). ¹H NMR (CDCl₃): δ = 7.1 (d, 2H, J_{HH} = 8.33 Hz, arom), 6.7 (d, 2H, J_{HH} = 8.3 Hz, arom), 5.3 (q, 1H, J_{HH} = 5.3 Hz, CH₃CHO₂), 3.8 (qd, 1H, J_{HH} = 7.1, 9.0 Hz, CH₃CHH'O), 3.5 (qd, 1H, J_{HH} = 7.1, 9.0 Hz, CH₃CHH'O), 2.3 (s, 3H, CH₃), 1.4 (d, 3H, J_{HH} = 5.3 Hz, CH₃CHO₂), 1.2 (t, 3H, J_{HH} = 7.1 Hz, CH₃CH₂O); ¹³C{¹H} NMR (CDCl₃): δ = 154.9, 131.2, 129.9, 117.5, 99.9, 61.5, 20.5, 20.4, 15.2; MS (ESI): m/z = 203.1067 (M+Na⁺).

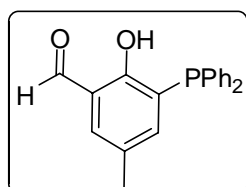
3-(diphenylphosphino)-2-(1-ethoxyethoxy)-5-methylbenzaldehyde:



To a solution of 1-(1-ethoxyethoxy)-4-methylbenzene (5.0 g, 27.7 mmol) and TMEDA (3.4 g, 29.1 mmol) in anhydrous diethyl ether (40 mL) *n*-butyllithium (2.5 M, 18.2 mL, 29.1 mmol) was added under argon, at room temperature. The orange suspension was stirred for 2 hours. The reaction mixture was cooled to -5 °C, and chlorodiphenylphosphine (6.8 g, 29.1 mmol) was added in a dropwise manner. The reaction mixture was allowed to warm to room temperature and stirred for 2 hours. *n*-Butyllithium (2.5 M, 22.5 mL, 36.0 mmol) was added under argon. The orange solution was stirred for 2 hours. The reaction mixture was cooled to -20 °C, and DMF (2.6 g, 36.0 mmol) was added. The reaction mixture was allowed to warm to room temperature and stirred for 1 hour. Water (30 mL) was added to quench the reaction. The organic phase was separated, and the aqueous phase was extracted with diethyl acetate. The combined organic phase was washed with water and brine, and then dried over MgSO₄. The solvents were evaporated in vacuo. The residue was triturated with methanol to afford 3-(diphenylphosphino)-2-(1-ethoxyethoxy)-5-methylbenzaldehyde as a light yellow solid (6.8 g, 17.3 mmol, 67% yield); ¹H NMR (CDCl₃): δ = 10.4 (s, 1H, CHO),

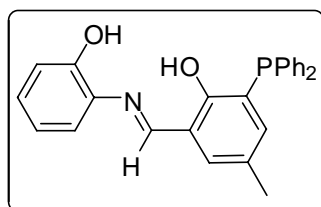
7.6 (d, $J_{\text{HH}} = 2.2$ Hz, 1H, arom), 7.4-7.2 (m, 10H, arom.), 6.8 (dd, $J_{\text{HH}} = 2.2$, $J_{\text{HP}} = 0.5$ Hz, 1H, arom), 5.3 (m, 1H, CH_3CHO_2), 3.3 (m, 2H, $\text{CH}_3\text{CHH}'\text{O}$), 2.2 (s, 3H, CH_3), 1.4 (d, 3H, $J_{\text{HH}} = 5.3$ Hz, CH_3CHO_2), 0.9 (t, 3H, $J_{\text{HH}} = 7.0$ Hz, $\text{CH}_3\text{CH}_2\text{O}$); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = -14.1$; MS (ESI): $m/z = 415.1$ ($\text{M} + \text{Na}^+$).

3-(diphenylphosphino)-2-hydroxy-5-methylbenzaldehyde:



To a solution of 3-(diphenylphosphino)-2-(1-ethoxyethoxy)-5-methylbenzaldehyde (13.2 g, 33.7 mmol) in ethanol (100 mL) TsOH (0.52 g, 2.0 mmol) was added at 40 °C. The yellow solution was allowed to cool to room temperature, and it was stirred for 1 hour. The solvent was evaporated and the resulting yellow oil was dissolved in ethyl acetate (50 mL). The organic solution was washed with water (2 x 20 mL), brine (20 mL), and then dried over MgSO_4 . The solvent was evaporated under vacuum. The residue was triturated with methanol to afford 3-(diphenylphosphino)-2-hydroxy-5-methylbenzaldehyde as a light yellow solid (8.0 g, 25 mmol, 74% yield). Mp 96.0 - 97.5 °C; ^1H NMR (CDCl_3) $\delta = 11.3$ (d, 1H, $J_{\text{HP}} = 3.3$ Hz, OH), 9.9 (d, 1H, $J_{\text{HP}} = 0.75$ Hz, CHO), 7.4-7.3 (m, 12H), 6.8 (dd, $J_{\text{HP}} = 4.5$ Hz, $J_{\text{HH}} = 2.0$ Hz, 1H, arom.), 2.2 (s, 3H, CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) $\delta = -15.0$; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) $\delta = 196.3$ (d, $J_{\text{CP}} = 1.5$ Hz), 161.0 (d, $J_{\text{CP}} = 16.8$ Hz), 141.7 (d, $J_{\text{CP}} = 1.5$ Hz), 135.5 (d, $J_{\text{CP}} = 10.2$ Hz), 134.3, 133.8 (d, $J_{\text{CP}} = 20.5$ Hz), 129.4, 128.9, 128.6 (d, $J_{\text{CP}} = 7.3$ Hz), 126.4 (d, $J_{\text{CP}} = 16.8$ Hz), 119.6 (d, $J_{\text{CP}} = 2.9$ Hz), 20.4; MS (ESI) m/z 321.1 ($\text{M} + \text{H}^+$).

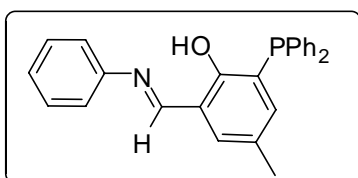
Synthesis of 1:



A mixture of 3-(diphenylphosphino)-2-hydroxy-5-methylbenzaldehyde (1.2 g, 3.8 mmol) and 2-aminophenol (0.41 g, 3.8 mmol) in dry toluene (20 mL) was heated at reflux for 3 hours over molecular sieves. The mixture was allowed to cool to room

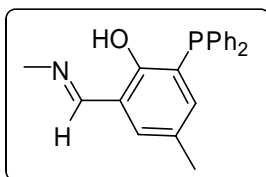
temperature, and the molecular sieves were filtered off. The toluene was evaporated in vacuo. The solid residue was recrystallized from methanol. Red crystalline material (1.25 g, 3.0 mmol, 80 % yield). ^1H NMR (CDCl_3) δ = 12.7 (br, 1H, OH), 8.7 (s, 1H, CH=N), 7.4 -7.3 (m, 10H, arom.), 7.24 (d, 1H, J_{HH} = 1.9 Hz, arom), 7.21 (td, J_{HH} = 1.4, 7.9 Hz, 1H, arom), 7.1 (dd, 1H, J_{HH} = 1.4, 7.8 Hz), 7.0 (dd, 1H, J_{HH} = 1.1, 7.9 Hz), 6.9 (td, J_{HH} = 1.1, 7.8 Hz, 1H, arom), 6.6 (dd, 1H, J_{HH} = 1.9, J_{HP} = 4.7 Hz), 5.7 (br, 1H, OH), 2.2 (s, 3H, CH₃.); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) = -15.18; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ = 163.5 (d, J_{CP} = 1.4 Hz), 160.0 (d, J_{CP} = 17.5 Hz), 150.0, 138.4, 135.9 (d, J_{CP} = 10.2 Hz), 135.5, 133.9 (d, J_{CP} = 19.8 Hz), 133.7, 129.0, 128.9, 128.8, 128.6, (d, J_{CP} = 7.3 Hz), 125.4 (d, J_{CP} = 14.6 Hz), 120.9, 118.3 (d, J_{CP} = 2.9 Hz), 118.2, 115.9, 20.5; MS (ESI): m/z = 412.1458 ($\text{M} + \text{H}^+$).

Synthesis of 2:



A mixture of 3-(diphenylphosphino)-2-hydroxy-5-methylbenzaldehyde (2.1 g, 6.5 mmol) and aniline (0.6 g, 6.5 mmol) in dry toluene (15 mL) was heated at reflux for 4 hours over molecular sieves. The mixture was allowed to cool to room temperature. The molecular sieves were filtered off, and the toluene was evaporated in vacuo. The solid residue was triturated in methanol, and then recrystallized from ethanol. Red crystalline material (2.3 g, 5.8 mmol, 89 %). Mp 150-151 °C; ^1H NMR (CDCl_3) δ = 13.7 (d, 1H, J_{HP} = 3.3 Hz, OH), 8.6 (s, 1H, CH=N), 7.4-7.3 (m, 12H, arom.), 7.3-7.2 (m, 4H, arom.), 6.6 (dd, J_{HH} = 2.0 Hz, J_{HP} = 4.8 Hz, 1H, arom), 2.1 (s, 3H, CH₃.); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ = -14.8; MS (ESI): m/z = 396.1502 ($\text{M} + \text{H}^+$).

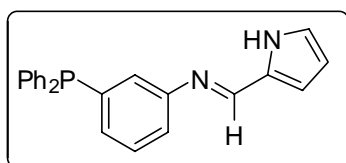
Synthesis of 3:



To solution of 3-(diphenylphosphino)-2-hydroxy-5-methylbenzaldehyde (2.0 g, 6.2 mmol) in ethanol (20 mL), over molecular sieves, methylamine (40 w/w% in water, 0.56 mL, 6.5 mmol) was added. The reaction mixture was stirred at room temperature

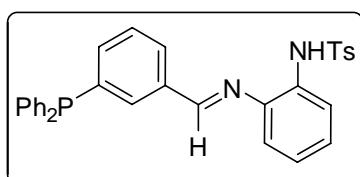
for six hours. The formation of a yellow precipitate was observed within minutes. At the end of the reaction the precipitate was dissolved adding CH_2Cl_2 (20 mL) to the reaction mixture. The molecular sieves were filtered off. The solvents were removed in vacuo. The solid residue was recrystallized from ethanol. Yellow crystalline material (1.7 g, 5.1 mmol, 81 %). ^1H NMR (CDCl_3) δ = 14.0 (s, 1H, OH), 8.3 (d, J_{HH} = 1.3 Hz, 1H, CH=N), 7.4-7.3 (m, 10H, arom.), 7.0 (d, J_{HH} = 1.9 Hz 1H, arom.), 6.5 (dd, J_{HH} = 1.9 Hz, J_{HP} = 4.6 Hz, 1H, arom), 3.4 (d, J_{HH} = 1.3 Hz, 3H, CH_3), 2.1 (s, 3H, CH_3 .); ^{31}P NMR (CDCl_3) δ = -14.6; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ = 165.8, 161.5 (d, J_{CP} = 17.5 Hz), 136.7, 136.0 (d, J_{CP} = 10.7 Hz), 133.9 (d, J_{CP} = 19.7 Hz), 132.0, 128.5, 128.3 (d, J_{CP} = 7.2 Hz), 127.2, 124.9 (d, J_{CP} = 12.4 Hz), 117.5, 45.4, 20.5; MS (ESI): m/z = 334.1 ($\text{M} + \text{H}^+$).

Synthesis of 4:



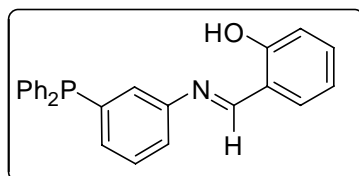
A mixture of 3-(diphenylphosphino)aniline (8.0 g, 28.8 mmol) and pyrrole-2-carboxaldehyde (2.8 g, 28.8 mmol) in dry toluene (50 mL) was heated at reflux for 12 hours over molecular sieves. The mixture was allowed to cool to room temperature, the molecular sieves were filtered off, and the toluene was evaporated in vacuo. The crude product was triturated with methanol for 5h at room temperature. Brown solid (8.9 g, 25.2 mmol, 87 %). Mp. 101-102 °C; ^1H NMR (CDCl_3) δ = 9.6 (br, 1H, NH), 8.1 (s, 1H, CH=N), 7.4-7.3 (m, 11H, arom.), 7.2-7.1 (m, 3H, arom.), 6.9 (brm, 1H, arom.), 6.7 (dd, J_{HH} = 1.3, 3.5 Hz, 1H, arom), 6.3 (dd, J_{HH} = 2.7, J_{HH} = 3.5 Hz, 1H, arom); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ = -1.8; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ = 149.8, 138.5 (d, J_{CP} = 12.4 Hz), 137.0 (d, J_{CP} = 10.9 Hz), 133.8 (d, J_{CP} = 19.0 Hz), 130.7 (d, J_{CP} = 19.0 Hz), 130.7, 129.3 (d, J_{CP} = 8.1 Hz), 128.7, 128.5 (d, J_{CP} = 7.3 Hz), 126.0 (d, J_{CP} = 20.5 Hz), 123.1, 121.3, 116.7, 110.5 ; MS (ESI) m/z 355.1355 ($\text{M} + \text{H}^+$).

Synthesis of 5:



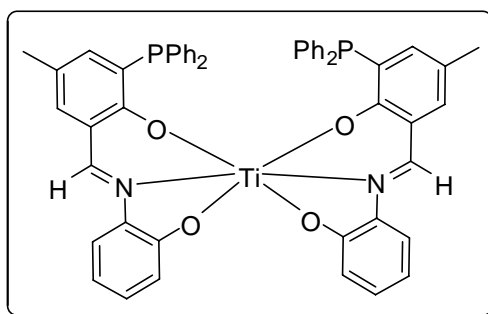
A mixture of 3-(diphenylphosphino)benzaldehyde (0.51 g, 1.8 mmol) and N-(2-aminophenyl)-4-methylbenzenesulfonamide (0.47 g, 1.8 mmol) in dry toluene (10 mL) was heated at reflux over molecular sieves for 3 hours. The mixture was allowed to cool to room temperature, the molecular sieves were filtered off, and the toluene was evaporated in vacuo. The solid residue was recrystallized from ethanol. White crystals (0.69 g, 1.2 mmol, 72%). ^1H NMR (CDCl_3) δ = 8.0 (s, 1H, CH=N), 7.8 (bm, 1H, arom.), 7.6-7.3 (m, 17H, arom.), 7.2 (td, 1H, J_{HH} = 1.1, 7.7 Hz), 7.0 (td, 1H, J_{HH} = 1.1, 7.7 Hz), 6.9 (m, 3H,) 2.2 (s, 3H,) ; ^{31}P $\{^1\text{H}\}$ NMR (CDCl_3) δ = -2.6; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ = 159.2, 143.5, 140.9, 138.8 (d, J_{CP} = 13.2 Hz), 137.0 (d, J_{CP} = 19.0 Hz), 136.4 (d, J_{CP} = 10.9 Hz), 136.0, 135.6, 134.3 (d, J_{CP} = 20.5 Hz), 133.8 (d, J_{CP} = 19.8 Hz), 132.2, 129.7 (d, J_{CP} = 13.9 Hz), 129.0 (d, J_{CP} = 6.5 Hz), 128.8 (d, J_{CP} = 7.3 Hz), 128.6, 127.7, 127.4, 127.1, 125.4, 121.6, 116.8, 21.4; MS (ESI): m/z = 535.1586 ($\text{M} + \text{H}^+$).

Synthesis of 6:



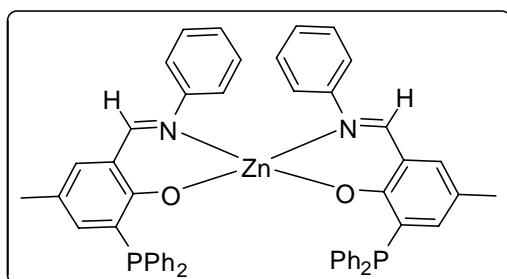
A mixture of 3-(diphenylphosphino)aniline (5.6 g, 20.3 mmol) and salicylaldehyde (2.5 g, 20.3 mmol) in dry toluene (30 mL) was heated at reflux over molecular sieves for 12 hours. The mixture was allowed to cool to room temperature, the molecular sieves were filtered off, and the toluene was evaporated in vacuo. The crude product was triturated with methanol for 5h at room temperature.. Yellow solid (6.5 g, 17.0 mmol, 84%). Mp 112-113 °C; ^1H NMR (CDCl_3): δ = 13.1 (br, 1H, OH), 8.5 (s, 1H, CH=N), 7.4-7.3 (m, 13H, arom.), 7.3-7.2 (m, 3H, arom.), 7.0 (d, 1H, arom.), 6.9 (td, J_{HH} = 1.0, 7.5 Hz, 1H, arom); ^{31}P $\{^1\text{H}\}$ NMR (CDCl_3) δ = -1.8; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ = 163.0, 161.5, 148.6 (d, J_{CP} = 8.0 Hz), 146.9, 139.2 (d, J_{CP} = 13.2 Hz), 136.7 (d, J_{CP} = 10.9 Hz), 133.7 (d, J_{CP} = 19.8 Hz), 133.3, 132.3, 132.0 (d, J_{CP} = 17.5 Hz), 129.5 (d, J_{CP} = 6.58 Hz), 128.9, 128.6 (d, J_{CP} = 7.3 Hz), 125.9 (d, J_{CP} = 21.2 Hz), 121.8, 119.1, 117.2. ; MS (ESI) m/z 382.1375 ($\text{M} + \text{H}^+$).

Synthesis of 7:



To a toluene (20 mL) solution of the ditopic ligand **1** (0.40 g, 0.98 mmol) $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.14 g, 0.49 mmol) was added at 60 °C. The reaction mixture was allowed to cool to room temperature and stirred for 3 hours. The product spontaneously precipitated from the solution. The red precipitate was filtered off, washed with pentane and dried in vacuum. Deep red solid (0.33 g, 0.37 mmol, 76%). Crystals of **7** suitable for X-ray structure determination were obtained by slow evaporation of the solvent from a CH_2Cl_2 solution of the compound. ^1H NMR (CDCl_3): δ = 8.2 (s, 1H, $\text{CH}=\text{N}$), 7.2-7.1 (m, 2H, arom), 7.1-6.9 (m, 11H, arom), 6.7 (td, J_{HH} = 1.0, 8.0 Hz, 1H, arom), 6.6 (dd, 1H, J_{HH} = 2.0, J_{HP} = 5.0 Hz), 6.4 (dd, 1H, J_{HH} = 1.0, 8.0 Hz), 2.2 (s, 3H, CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) = -10.8; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ = 163.3 (d, J_{CP} = 14.6 Hz), 161.8, 155.5, 140.7 (d, J_{CP} = 6.6 Hz), 138.6, 136.6 (d, J_{CP} = 11.7 Hz), 136.4 (d, J_{CP} = 11.7 Hz), 134.1 (d, J_{CP} = 13.2 Hz), 133.8, 133.3 (d, J_{CP} = 20.5 Hz), 129.9, 128.8 (d, J_{CP} = 1.4 Hz), 125.5 (d, J_{CP} = 13.2 Hz), 120.9 (d, J_{CP} = 2.2 Hz), 118.9, 114.8, 114.2, 20.5; MS (MALDI): m/z = 866.1931 (M^+).

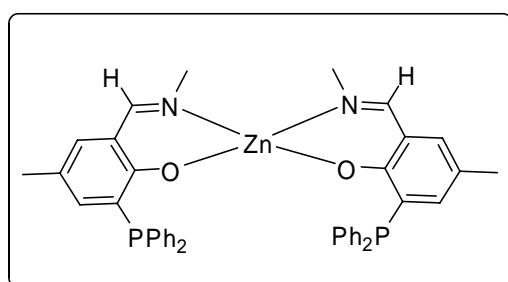
Synthesis of 8:



To a suspension of the phosphine **2** (0.39 g 1.0 mmol) in dry hexane (20 mL) dry THF was added until a homogenous solution had been obtained (11 mL THF). To the resulting clear solution $\text{Zn}[\text{N}(\text{Si}(\text{CH}_3)_3)_2]_2$ (0.2 M in THF, 2.5 mL, 0.5 mmol) was added. The formation of a yellow precipitate was observed in a few minutes. The suspension was stirred at room temperature for 2 hours. The precipitate was isolated by

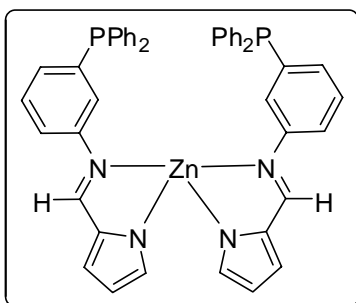
filtration, washed with hexane/THF (8:2) and pentane. Yellow solid (0.38 g, 0.44 mmol, 88%). Crystals of **8** suitable for X-ray structure determination were obtained by layering cyclohexane on the top of a CH₂Cl₂ solution of the compound. ¹H NMR (400 MHz, CDCl₃) δ = 8.1 (s, 1H, CH=N), 7.4-7.2 (m, 10H, arom.), 7.1-7.0 (m, 3H, arom.), 6.9 (dr, 1H, arom), 6.7-6.6 (m, 3H, arom), 2.1 (s, 3H, CH₃); ³¹P{¹H} NMR δ = -13.7; MS (MALDI) m/z = 852.2004.

Synthesis of **9**:



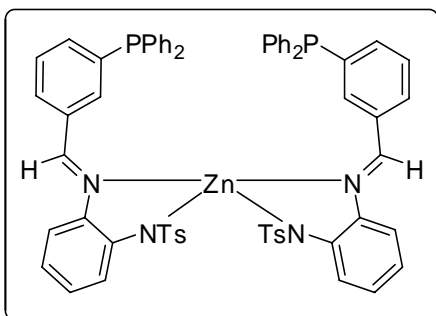
To a suspension of the phosphine **3** (0.32 g, 0.96 mmol) in dry hexane (15 mL) dry THF was added until a homogenous solution had been obtained (3 mL THF). To the resulting clear solution Zn[N(Si(CH₃)₃)₂]₂ (0.096 M in THF, 5.0 mL, 0.48 mmol) was added. The formation of a yellow precipitate was observed in a few minutes. The suspension was stirred at room temperature for 2 hours. The precipitate was isolated by filtration, washed with hexane/THF (8:2) and pentane. Yellow solid (0.31 g, 0.43 mmol, 90 %). Crystals of **9** suitable for X-ray structure determination were obtained by layering cyclohexane on the top of a CH₂Cl₂ solution of the compound. ¹H NMR (CDCl₃): δ = 7.9 (s, 1H, CH=N), 7.3-7.2 (m, 10H, arom.), 6.8 (br, 1H, arom.), 6.7 (dd, *J*_{HH} = 2.5 Hz, *J*_{HP} = 4.3 Hz, 1H, arom), 2.7 (s, 3H, CH₃), 2.0 (s, 3H, CH₃); ³¹P{¹H} NMR δ = -13.5; ¹³C{¹H} NMR (CDCl₃): δ = 171.3 (d, *J*_{CP} = 0.4 Hz), 169.2 (d, *J*_{CP} = 16.8 Hz), 139.2, 138.3 (d, *J*_{CP} = 11.9 Hz), 135.8, 134.0 (d, *J*_{CP} = 20.5 Hz), 130.5 (d, *J*_{CP} = 5.1 Hz), 128.0 (d, *J*_{CP} = 12.2 Hz), 128.0, 122.8, 116.7 (d, *J*_{CP} = 2.2 Hz), 46.4, 20.2.

Synthesis of 10:



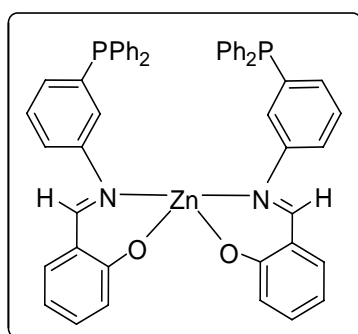
To a suspension of the phosphine **4** (0.47 g, 1.3 mmol) in dry hexane (20 mL) dry THF was added until a homogenous solution had been obtained (4 mL THF). To the resulting clear solution $\text{Zn}[\text{N}(\text{Si}(\text{CH}_3)_3)_2]_2$ (0.096 M in hexane, 7 mL, 0.67 mmol) was added. Precipitation of a yellow solid was observed in a few minutes. The suspension was stirred at room temperature for 2 hours. The precipitate was isolated by filtration, washed with hexane/THF (8:2) and pentane. Yellow solid (0.43 g, 0.56 mmol, 84 %). Crystals of **10** suitable for X-ray structure determination were obtained by layering cyclohexane on the top of a CH_2Cl_2 solution of the compound. ^1H NMR (CDCl_3) δ = 8.1 (s, 1H, $\text{CH}=\text{N}$), 7.3-7.0 (m, 15H, arom.), 6.9 (dd, J_{HH} = 1.0, 3.7 Hz, 1H, arom); 6.4 (dd, J_{HH} = 1.6, 3.7 Hz, 1H, arom); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ = -1.4; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ = 154.2, 147.0 (d, J_{CP} = 5.8 Hz), 139.9 (d, J_{CP} = 13.2 Hz), 138.4, 137.9, 137.3 (d, J_{CP} = 10.9 Hz), 133.9 (d, J_{CP} = 19.8 Hz), 131.4 (d, J_{CP} = 24.2 Hz), 129.9 (d, J_{CP} = 8.7 Hz), 129.1, 128.9 (d, J_{CP} = 7.0 Hz), 126.1 (d, J_{CP} = 16.1 Hz), 121.5, 120.5, 115.1. MS (MALDI): m/z = 770.1706 (M^+).

Synthesis of 11:



To a suspension of the phosphine **5** (0.21 g, 0.4 mmol) in dry hexane (20 mL) dry THF was added until a homogenous solution had been obtained (10 mL THF). To the resulting clear solution $\text{Zn}[\text{N}(\text{Si}(\text{CH}_3)_3)_2]_2$ (0.2 M in THF, 1 mL, 0.2 mmol) was added. The product started to precipitate in a few minutes. The suspension was stirred at room temperature for 2 hours. The yellow precipitate was filtered and washed with hexane/THF (8:2) and pentane. Yellow solid (0.19 g, 0.17 mmol, 84 %). Crystals of **11** suitable for X-ray structure determination were obtained by layering cyclohexane on the top of a CH_2Cl_2 solution of the compound. Mp 278 °C. ^1H NMR (400 MHz, 25 °C, CDCl_3) δ = 8.4 (s, 1H, CH=N), 8.0-7.9 (m, 3H, arom.), 7.3-6.9 (m, 18H, arom), 6.7 (td, 1H, J_{HH} = 1.5, 5.6 Hz), 2.2 (s, 3H, CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ = -2.9; MS (MALDI): m/z = 1131.2256 ($\text{M} + \text{H}^+$).

Synthesis of **12**:



To a suspension of the phosphine **6** (0.29 g 0.77 mmol) in dry hexane (20 mL) dry THF was added until a homogenous solution had been obtained (4 mL THF). To the resulting clear solution $\text{Zn}[\text{N}(\text{Si}(\text{CH}_3)_3)_2]_2$ (0.1 M in THF, 4.0 mL, 0.40 mmol) was added. The formation of a yellow precipitate was observed within minutes. The suspension was stirred at room temperature for 2 hours. The precipitate was isolated by filtration, washed with hexane/THF (4:1) and pentane. Yellow solid (0.28 g, 0.34 mmol, 88%). Mp 175 °C. Crystals of **12** suitable for X-ray structure determination were obtained by layering cyclohexane on the top of a CH_2Cl_2 solution of the compound. ^1H NMR (400 MHz, CDCl_3) δ = 8.0 (s, 1H, CH=N), 7.3 (td, J_{HH} = 2.0, 7.0 Hz, 1H, arom), 7.3-6.9 (m, 14H, arom.), 6.8 (d, J_{HH} = 8.4 Hz, 1H, arom.), 6.6 (td, J_{HH} = 1.0, 7.1 Hz, 1H, arom); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ = -1.6; $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ = 172.5, 170.0, 149.0 (d, J_{CP} = 6.6 Hz), 140.4 (d, J_{CP} = 14.6 Hz), 137.3, 136.9 (d, J_{CP} = 10.9 Hz), 136.7, 133.9 (d, J_{CP} = 19.8 Hz), 132.5 (d, J_{CP} = 20.4 Hz), 130.3 (d, J_{CP} = 7.3 Hz), 129.2, 128.9

(d, $J_{\text{CP}} = 7.3$ Hz), 126.8 (d, $J_{\text{CP}} = 19.8$ Hz), 123.7, 121.5, 118.7, 115.4; MS (MALDI) m/z 824.1686 (M^+).

Zinc bis[bis(trimethylsilyl)amide]

A mixture of ZnCl_2 and sodium bis-(trimethylsilyl)amide was refluxed in dry diethylether (100 mL) for 5h. The reaction mixture was filtered through a pad of celite. The solvent was removed in vacuum, and the crude product was purified by distillation (bp 65°C , 8×10^{-2} mbar). Colourless liquid (21.3 g, 55.4 mmol, 86%). ^1H NMR (400 MHz, CDCl_3) $\delta = 0.1$ (s), MS (IQ+ve) m/z 369.1012 ($\text{M}-\text{CH}_3$).

General Procedure for the hydroformylation of 1-octene

The autoclaves were purged with 20 bar of syngas (CO/H_2 1:1 v/v) five times at 90°C , and five times at 30°C . Toluene solutions of $[\text{Rh}(\text{acac})(\text{CO})_2]$ (2 mg, 8 μmol in 2.4 mL of toluene) and the corresponding ligand (2, 4, 10 or 20 eq in 2.4 mL of toluene) were injected into the autoclave. As a catalyst pretreatment, the autoclave was pressurized with 20 bar of syngas at 80°C for 3 hours. The pressure was released, and stock solution of the substrate (3.2 mL of stock solution: 0.84 mL of 1-octene and 0.17 mL of decane as internal standard in 2.18 mL of toluene) was added to the reaction mixture. The pressure was adjusted to 10 bar (CO/H_2 , 1:1). The reaction was followed by monitoring the gas consumption, and by GC analysis of the samples taken over the course of the reaction. Turn over frequencies were calculated at 40% of conversion.

HP-FT-IR Experiments.

High-pressure IR experiments were performed in a 50 mL autoclave (SS 316) equipped with IRTRAN windows (ZnS , transparent up to 700 cm^{-1} , i.d. 10 mm, optical path length = 0.4 mm), a mechanical stirrer, a temperature controller, and a pressure transducer. In a typical experiment 5 mg of $\text{Rh}(\text{acac})(\text{CO})_2$ and 2, 4, 10 or 20 equiv of ligand were stirred in 15 mL of cyclohexane under argon. The reaction mixture was transferred into the purged autoclave and the autoclave was pressurized with 20 bar of CO/H_2 (1/1). The autoclave was placed in the infrared spectrometer and heated to 80°C . IR spectra were recorded while the sample was being stirred.