

Supporting Information

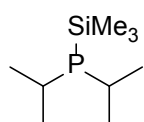
A Simple Route to Azaborinylphosphines: Isoelectronic B-N Analogues of Arylphosphine Ligands

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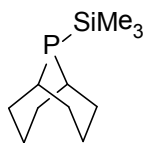
General considerations

Unless otherwise stated, all manipulations were carried out under a dry N₂ or argon atmosphere using standard Schlenk line and glove-box techniques. Toluene, *n*-hexane, diethyl ether, dichloromethane and tetrahydrofuran were purified by means of a Grubbs type solvent system and deoxygenated by three successive freeze-pump-thaw cycles. Cyclohexene and deuterated benzene (C₆D₆) and dichloromethane (CD₂Cl₂) were stirred with CaH₂ overnight, distilled, deoxygenated by three freeze-pump-thaw cycles and stored over 4 Å molecular sieves. NMR spectra were acquired on Jeol ECP (Eclipse) 300, Jeol ECS 300, Varian 400-MR, Jeol ECS 400 and Varian VNMR500 spectrometers. Chemical shifts are referenced relative to high frequency of residual solvent (¹H and ¹³C), 85% H₃PO₄ (³¹P) and BF₃·OEt₂ (¹¹B). Elemental analyses were carried out by the Microanalytical Laboratory at the University of Bristol. Mass spectrometry was carried out by the Mass Spectrometry Service at the University of Bristol. 9-aza-10-bora-10-chlorophenanthrene (**1**),¹ *s*-PhobPH² and *s*-PhobPCl were synthesised according to literature methods. All other reagents were used as received from Sigma-Aldrich, Acros or Strem Chemicals.

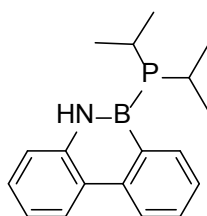


Di-isopropyl(trimethylsilyl)phosphine.³ This was prepared by a modification of the literature procedure. To a stirred solution of ⁱPr₂PH (2.39 g, 20.2 mmol) in THF (20 mL), cooled to -78 °C, was added a 1.6 M solution of ⁿBuLi in hexane (13.3 mL, 21.2 mmol) dropwise over 5 min. After complete addition, the solution was stirred at RT for 2 h. The reaction mixture was then cooled to -78 °C and SiMe₃Cl (2.5 mL, 20.2 mmol) was added dropwise over 10 min. The mixture was left to warm to RT overnight. The solvent was then removed *in vacuo* and the residue distilled to afford the product as a

pyrophoric colourless oil (2.19 g, 11.5 mmol, 57%). $^{31}\text{P}\{^1\text{H}\}$ NMR (122 MHz, C_6D_6) $\delta = -44.0$. HR-MS (EI) m/z calculated for $\text{C}_9\text{H}_{23}\text{PSi}$ $[\text{M}]^+ = 190.1307$; obs.: 190.1304.

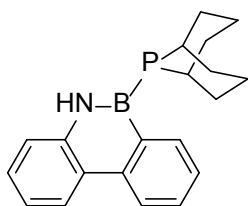


Trimethylsilyl-9-phoshabicyclo[3.1.1]nonane. To a stirred solution of *s*-PhobPH (5.00 g, 35.2 mmol) in THF (20 mL), cooled to $-78\text{ }^\circ\text{C}$, was added a 1.6 M solution of $^n\text{BuLi}$ in hexane (23.1 mL, 36.9 mmol) over 5 min. After addition was completed, the solution was stirred at RT for a further 2 h. The resulting suspension was then cooled to $-78\text{ }^\circ\text{C}$ again and Me_3SiCl (4.46 mL, 35.1 mmol) added via a dropping funnel over 20 min. Extra THF (20 mL) was added to facilitate the stirring. The reaction mixture was then allowed to warm to RT overnight. All the volatile components were removed *in vacuo* to give a cloudy oil. The product was distilled as a colourless oil which slowly solidified as a white crystalline solid (4.71 g, 22.0 mmol, 63%). The crystals were of suitable quality for X-ray diffraction. $^{31}\text{P}\{^1\text{H}\}$ NMR (122 MHz, C_6D_6) $\delta = -67.4$. ^1H NMR (400 MHz, C_6D_6) $\delta = 2.32\text{--}2.22$ (2H, m, PhobP- CH_2), 2.05-1.54 (12H, m, PhobP- CH/CH_2), 0.24 (9H, d, $^3J_{\text{HP}} = 4.9$ Hz, SiCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6) $\delta = 34.2$ (d, $J_{\text{CP}} = 10.0$ Hz, PhobP- CH_2), 31.2 (d, $J_{\text{CP}} = 5.0$ Hz, PhobP- CH_2), 24.0 (d, $J_{\text{CP}} = 7.1$ Hz, PhobP- CH_2), 23.3 (d, $J_{\text{CP}} = 11.7$ Hz, PhobP- CH), 22.7 (d, $J_{\text{CP}} = 1.7$ Hz, PhobP- CH_2), 0.39 (d, $J_{\text{CP}} = 14.2$ Hz, SiCH_3). **Anal.** Found (calcd for $\text{C}_{11}\text{H}_{23}\text{PSi}$): C, 62.13 (61.63), H, 10.57 (10.82). HR-MS (EI) m/z calculated for $\text{C}_{11}\text{H}_{23}\text{PSi}$ $[\text{M}]^+ = 214.1307$; obs.: 214.1309.

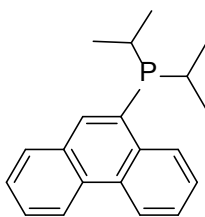


9-aza-10-bora-10-diisopropylphosphenanthrene (L_{1a}). To a solution of 9-aza-10-bora-10-chlorophenanthrene **1** (0.311 g, 1.46 mmol) in CH_2Cl_2 (5 mL) was added a solution of $^i\text{Pr}_2\text{PSiMe}_3$ (0.277 g, 1.46 mmol) in CH_2Cl_2 (5 mL) at RT. After 10 min stirring the reaction mixture at RT, the volatile compounds were removed *in vacuo* to give a colourless viscous oil in quantitative yield. Trituration with hexane afforded the product as a white sticky solid (0.250 g, 0.847 mmol, 58%). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2) $\delta = -49.1$ (br s). $^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, CD_2Cl_2) $\delta = 40.8$ (br s). ^1H NMR (500 MHz, CD_2Cl_2) $\delta = 8.59\text{--}8.56$ (1H, m, ar. CH), 8.51 (, $J = 8.2$ Hz, ar. CH), 8.48 (1H, dm, $J = 8.1$ Hz, ar. CH), 7.97 (1H, br s, NH), 7.80-7.77 (1H, m, ar. CH), 7.60-7.57 (1H, m, ar. CH), 7.51-7.47 (1H, m, ar. CH), 7.41-7.39 (1H, m, ar. CH), 7.35-7.32 (1H, m, ar. CH), 2.35 (2H, heptd, $^3J_{\text{HH}} = 7.0$ Hz, $^2J_{\text{PH}} = 3.9$ Hz, $^i\text{Pr-CH}$), 1.30-1.26 (6H, m, $^i\text{Pr-CH}_3$), 1.17-1.12 (6H, m, $^i\text{Pr-CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2) $\delta = 138.9$ (d, $J = 2.5$ Hz, quat. C), 137.8 (d, $J = 4.4$ Hz, quat. C), 137.6 (d, $J = 12.8$ Hz, ar. CH), 131.8 (d, $J = 1.2$ Hz, ar. CH), 128.6 (ar. CH), 126.6 (ar. CH), 124.5 (ar. CH), 124.3 (quat. C), 122.8 (ar. CH), 122.6 (d, $J = 1.5$ Hz, ar. CH), 119.8 (ar. CH),

22.8 (d, $J = 12.7$ Hz, $^i\text{Pr-CH}_3$), 21.8 (d, $J = 10.8$ Hz, $^i\text{Pr-CH}$) (one quaternary carbon from aromatic region not observed).

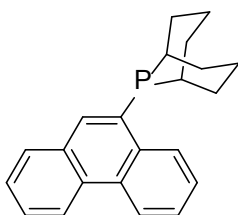


9-aza-10-bora-10-(sym-phobyl)phosphinophenanthrene (L_{1b}). To a solution of 9-aza-10-bora-10-chlorophenanthrene **1** (0.505 g, 2.37 mmol) in CH_2Cl_2 (10 mL) was added a solution of PhobPSiMe₃ (0.507 g, 2.37 mmol) in CH_2Cl_2 (10 mL) at RT. After 10 min stirring the reaction mixture at RT, the volatile compounds were removed *in vacuo* to afford L_{1b} as a white solid (0.695 g, 2.18 mmol, 92%). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2) $\delta = -64.5$ (br s). $^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, CD_2Cl_2) $\delta = 41.1$ (br s). ^1H NMR (500 MHz, CD_2Cl_2) $\delta = 8.48$ (1H, dm, $J = 8.3$ Hz, ar. CH), 8.41 (1H, dm, $J = 8.0$ Hz, ar. CH), 8.19 (1H, dm, $J = 7.6$ Hz, ar. CH), 7.76-7.73 (1H, m, ar. CH) 7.63 (1H, br s, NH), 7.52-7.49 (1H, m, ar. CH), 7.45-7.42 (1H, m, ar. CH), 7.29-7.26 (2H, m, ar. CH), 2.65 (2H, br s, PhobP-CH), 2.37 (2H, br s, PhobP-CH₂), 2.19-1.83 (9H, br m, PhobP-CH₂), 1.43 (1H, br s, PhobP-CH₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2) $\delta = 139.2$ (quat. C), 137.6 (quat. C), 135.8 (ar. CH), 131.6 (ar. CH), 128.6 (ar. CH), 126.7 (ar. CH), 124.5 (ar. CH), 123.8 (quat. C), 123.0 (ar. CH), 122.2 (ar. CH), 119.4 (ar. CH), 33.8 (d, $J_{\text{CP}} = 9.5$ Hz, PhobP-CH₂), 31.1 (s, PhobP-CH₂), 25.1 (d, $J_{\text{CP}} = 5.9$ Hz, PhobP-CH), 23.1 (br s, PhobP-CH₂) (one quaternary carbon from aromatic region not observed). **Anal.** Found (calcd for $\text{C}_{20}\text{H}_{23}\text{BNP}$): C, 75.21 (75.26), H, 7.20 (7.26), N, 4.52 (4.39).

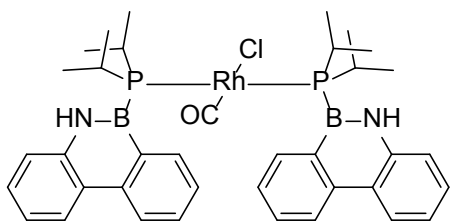


9-Diisopropylphosphinophenanthrene (L_{2a}). To a stirred solution of 9-bromophenanthrene (0.935 g, 3.64 mmol) in THF (40 mL) cooled to -60 °C was added a 1.6 M solution of $^n\text{BuLi}$ in hexane (2.39 mL, 3.82 mmol) over 5 min. The resulting orange solution was stirred at -60 °C for 20 min after which $^i\text{Pr}_2\text{PCl}$ (0.61 mL, 3.82 mmol) was added dropwise. The solution was left to reach RT overnight, during which the solution became yellow. The volatile compounds were removed *in vacuo* and the yellow solid was dissolved in toluene (50 mL) and filtered through silica. After removal of the toluene *in vacuo*, the resulting yellow residue was washed with hexane (3×5 mL) at -78 °C to afford the product as a pale yellow solid (0.757 g, 2.57 mmol, 71%). Crystals suitable for X-ray diffraction were obtained by recrystallization from a hot mixture of hexane/methanol (50/50). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) $\delta = -7.2$ (br s, upon cooling to -60 °C the signal gets sharper). ^1H NMR (400 MHz, CD_2Cl_2) $\delta = 9.03$ -8.98 (1H, br m, ar. CH), 8.77-8.74 (1H, m, ar. CH), 8.71 (1H, dm, $J = 8.2$ Hz, ar. CH), 7.95-7.91 (2H, m, ar. CH), 7.71-7.62 (4H, m, ar. CH), 2.34 (2H,

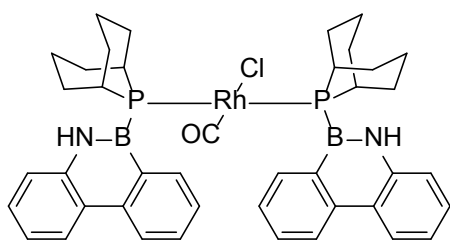
heptd, $^3J_{\text{HH}} = 7.0$ Hz, $^2J_{\text{PH}} = 1.5$ Hz, $^i\text{Pr-CH}$), 1.18 (6H, dd, $J = 14.8, 7.0$ Hz, $^i\text{Pr-CH}_3$), 1.02 (6H, dd, $J = 12.0, 7.0$ Hz, $^i\text{Pr-CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2) $\delta = 136.6$ (d, $J_{\text{CP}} = 21.2$ Hz, quat. C), 133.1 (ar. CH), 132.3 (d, $J_{\text{CP}} = 22.5$ Hz, quat. C), 131.7 (quat. C), 131.1 (quat. C), 130.7 (d, $J_{\text{CP}} = 4.0$ Hz, quat. C), 129.2 (ar. CH), 128.2 (d, $J = 31.5$ Hz, ar. CH), 127.7 (ar. CH), 127.2 (ar. CH), 126.9 (d, $J_{\text{CP}} = 1.8$ Hz, ar. CH), 126.8 (d, $J = 2.3$ Hz, ar. CH), 123.4 (ar. CH), 123.0 (ar. CH), 24.2 (d, $^1J_{\text{CP}} = 13.1$ Hz, $^i\text{Pr-CH}$), 20.7 (d, $^2J_{\text{CP}} = 18.1$ Hz, $^i\text{Pr-CH}_3$), 19.5 (d, $^2J_{\text{CP}} = 10.1$ Hz, $^i\text{Pr-CH}_3$). **Anal.** Found (calcd for $\text{C}_{20}\text{H}_{23}\text{P}$): C, 82.44 (81.60), H, 7.79 (7.88). **HR-MS** (EI) m/z calculated for $\text{C}_{20}\text{H}_{23}\text{P} [\text{M}]^+ = 294.1537$; obs.: 294.1541.



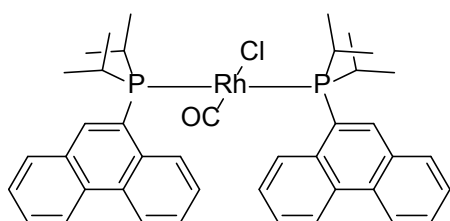
9-(Sym-phobyl)phosphinophenanthrene ($\text{L}_{2\text{b}}$). To a stirred solution of 9-bromophenanthrene (1.98 g, 7.70 mmol) in THF (80 mL) cooled to -60 °C was added a 1.6 M solution of $^n\text{BuLi}$ in hexane (4.81 mL, 7.70 mmol) over 5 min. The yellow solution was stirred at -50 °C for 20 min after which a solution of *s*-PhobPCl (1.05 g, 5.92 mmol) in THF (10 mL) was added dropwise over 5 min. The solution was allowed to reach RT overnight, during which time the solution turned a dark brown. ^{31}P NMR spectroscopy indicated that the reaction had proceeded to 80% conversion. The volatiles were removed *in vacuo* to give a brown sticky residue. Toluene (25 mL) was added and the suspension filtered through silica. Removal of the toluene *in vacuo* gave a yellow oil which upon washing with hexane (3×7 mL) at -78 °C gave $\text{L}_{2\text{b}}$ as a yellow powder (1.235 g, 3.88 mmol, 66%). Recrystallisation from hot hexane in air yielded co-crystals of $\text{L}_{2\text{b}}$ and the corresponding phosphine oxide, as determined by X-ray diffraction. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2) $\delta = -23.8$ (s). ^1H NMR (500 MHz, CD_2Cl_2) $\delta = 8.75$ (1H, dm, $J = 8.3$ Hz, ar. CH), 8.67 (1H, dm, $J = 8.0$ Hz, ar. CH), 8.27 (1H, dm, $J = 8.1$ Hz, ar. CH), 7.88-7.86 (1H, m, ar. CH), 7.78 (1H, d, $J = 4.1$ Hz, ar. CH), 7.69-7.59 (4H, m, ar. CH), 2.74 (2H, s, PhobP-CH), 2.47-1.72 (11H, m, PhobP- CH_2), 1.41-1.36 (1H, m, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2) $\delta = 135.8$ (d, $J_{\text{CP}} = 32.2$ Hz, quat. C), 133.5 (d, $J_{\text{CP}} = 12.3$ Hz, quat. C), 132.0 (d, $J_{\text{CP}} = 1.6$ Hz, quat. C), 131.4 (d, $J_{\text{CP}} = 5.4$ Hz, ar. CH), 130.7 (d, $J_{\text{CP}} = 2.5$ Hz, quat. C), 130.4 (quat. C), 128.8 (d, $J_{\text{CP}} = 1.1$ Hz, ar. CH), 127.4 (ar. CH), 127.1 (ar. CH), 127.0 (ar. CH), 126.8 (d, $J_{\text{CP}} = 1.7$ Hz, ar. CH), 126.7 (d, $J_{\text{CP}} = 15.8$ Hz, ar. CH), 123.9 (d, $J_{\text{CP}} = 1.3$ Hz, ar. CH), 123.0 (ar. CH), 33.0 (d, $J_{\text{CP}} = 15.3$ Hz, PhobP- CH_2), 26.8 (d, $J_{\text{CP}} = 12.4$ Hz, PhobP-CH), 26.1 (d, $J_{\text{CP}} = 4.5$ Hz, PhobP- CH_2), 23.7 (d, $J_{\text{CP}} = 5.3$ Hz, PhobP- CH_2), 22.5 (d, $J_{\text{CP}} = 1.5$ Hz, PhobP- CH_2). **Anal.** Found (calcd for $\text{C}_{22}\text{H}_{23}\text{P}$): C, 82.57 (82.99), H, 7.38 (7.28). **HR-MS** (EI) m/z calculated for $\text{C}_{22}\text{H}_{23}\text{P} [\text{M}]^+ = 318.1537$; obs.: 318.1534.



trans-[RhCl(CO)(L_{1a})₂] (3a). A solution of **L_{1a}** (20.0 mg, 0.068 mmol) in CH₂Cl₂ (0.4 mL) was added to a solution of [RhCl(CO)₂]₂ (6.6 mg, 0.017 mmol) in CH₂Cl₂ (0.4 mL). Evolution of CO gas was observed. Once the evolution of CO had stopped, the solvent was removed *in vacuo* to afford the Rh(I) complex **3a** in quantitative yield. Crystals suitable for X-ray diffraction were obtained by layering a CH₂Cl₂ solution of **3a** with hexane at RT. ³¹P{¹H} NMR (202 MHz, CD₂Cl₂) δ = 0.8 (br d, *J*_{PRh} ≈ 120 Hz). ¹¹B{¹H} NMR (96 MHz, CD₂Cl₂) δ = 36.9 (br s). ¹H NMR (500 MHz, CD₂Cl₂) δ = 9.15 (2H, d, *J* = 7.7 Hz, ar. CH), 8.64 (2H, br s, NH), 8.53 (2H, d, *J* = 8.3 Hz, ar. CH), 8.49 (2H, dm, *J* = 8.1 Hz, ar. CH), 7.81-7.78 (2H, m, ar. CH), 7.57-7.54 (2H, m, ar. CH), 7.49-7.46 (2H, m, ar. CH), 7.38-7.31 (4H, m, ar. CH), 2.84 (4H, br m, ⁱPr-CH), 1.48-1.43 (12H, m, ⁱPr-CH₃), 1.37-1.33 (12H, m, ⁱPr-CH₃). **Anal.** Found (calcd for C₃₇H₄₆B₂ClN₂OP₂Rh): C, 58.38 (58.73), H, 5.96 (6.13), N, 3.79 (3.70). **IR** spectrum (CH₂Cl₂): 1951 cm⁻¹ ν(CO).

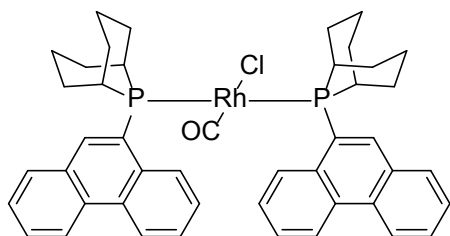


trans-[RhCl(CO)(L_{1b})₂] (3b). A solution of **L_{1b}** (25.6 mg, 0.080 mmol) in CH₂Cl₂ (0.4 mL) was added to a solution of [RhCl(CO)₂]₂ (7.8 mg, 0.020 mmol) in CH₂Cl₂ (0.4 mL). Upon addition, the solution went dark brown and a solid precipitated out of solution. The supernatant was syringed off and the solid washed with CH₂Cl₂ (2 × 1 mL) to afford the product as an orange solid (7.0 mg, 0.0069 mmol, 22%). Crystals of **3b** suitable for X-ray diffraction were obtained by layering a CH₂Cl₂ solution of [RhCl(CO)₂]₂ with a CH₂Cl₂ solution of **L_{1b}**. ³¹P{¹H} NMR (202 MHz, CD₂Cl₂) δ = -17.6 (d, *J*_{PRh} ≈ 120 Hz). ¹H NMR (500 MHz, CD₂Cl₂) δ = 8.35 (2H, br d, *J* = 8.1 Hz, ar. CH), 8.30 (2H, dm, *J* = 8.1 Hz, ar. CH), 8.20 (2H, br s, NH), 8.07 (2H, dm, *J* = 7.6 Hz, ar. CH), 7.66-7.63 (2H, m, ar. CH), 7.38-7.32 (4H, m, ar. CH), 7.24-7.18 (4H, m, ar. CH), 2.99-2.96 (6H, m, PhobP-H), 2.50 (4H, br s, PhobP-H), 2.12-1.28 (18H, m, PhobP-H). **Anal.** Found (calcd for C₄₁H₄₆B₂ClN₂OP₂Rh·CH₂Cl₂): C, 56.71 (56.70), H, 5.76 (5.44), N, 3.88 (3.15). **IR** spectrum (CH₂Cl₂): 1946 cm⁻¹ ν(CO).



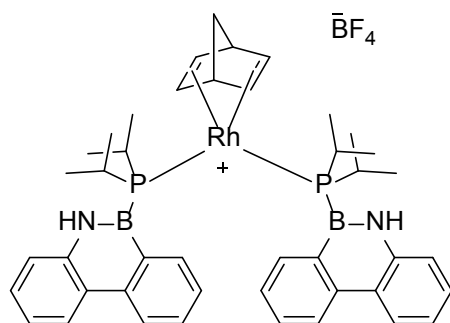
trans-[RhCl(CO)(L_{2a})₂] (4a). A solution of **L_{2a}** (15 mg, 0.051 mmol) in CH₂Cl₂ (0.4 mL) was added to a solution of [RhCl(CO)₂]₂ (5.0 mg, 0.013 mmol) in

CH₂Cl₂ (0.4 mL). After a few minutes, a yellow solid started precipitating out of solution. The solvent was removed *in vacuo* to afford **4a** as a yellow solid in quantitative yield. Crystals of **4a** suitable for X-ray diffraction were obtained by layering a CH₂Cl₂ solution of [RhCl(CO)₂]₂ with a CH₂Cl₂ solution of **L_{2a}**. ³¹P{¹H} NMR (202 MHz, CD₂Cl₂) δ = 33.8 (d, ¹J_{PRh} = 121 Hz). ¹H NMR (500 MHz, CD₂Cl₂) δ = 10.35 (2H, br s, ar. CH), 8.77-8.75 (2H, m, ar. CH), 8.72 (2H, d, *J* = 8.3 Hz, ar. CH), 8.01-7.98 (4H, m, ar. CH), 7.76-7.65 (8H, m, ar. CH), 3.05 (4H, br s, ⁱPr-CH), 1.41 (12H, br s, ⁱPr-CH₃), 1.27 (12H, br s, ⁱPr-CH₃). **Anal.** Found (calcd for C₄₁H₄₆ClOP₂Rh): C, 64.68 (65.21), H, 6.13 (6.14). **HR-MS (ESI)** *m/z* calculated for C₄₁H₄₆OP₂Rh [M - Cl]⁺ = 719.2073; obs.: 719.2086. **IR** spectrum (CH₂Cl₂): 1966 cm⁻¹ ν(CO).



trans-[RhCl(CO)(L_{2b})₂] (4b). A solution of **L_{2b}** (15 mg, 0.047 mmol) in CH₂Cl₂ (0.4 mL) was added to a solution of [RhCl(CO)₂]₂ (4.6 mg, 0.012 mmol) in CH₂Cl₂ (0.4 mL). After a few minutes, a yellow solid began precipitating out of solution. The solvent was

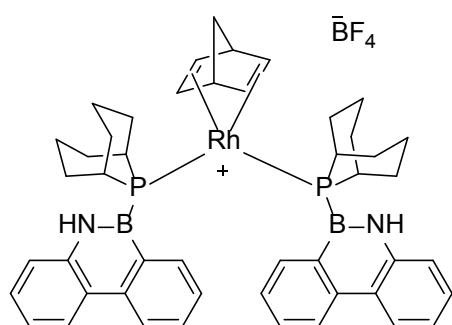
removed *in vacuo* to afford **4b** as a yellow solid in quantitative yield. Crystals of **4b** suitable for X-ray diffraction were obtained by layering a CH₂Cl₂ solution of [RhCl(CO)₂]₂ with a CH₂Cl₂ solution of **L_{2b}**. ³¹P{¹H} NMR (202 MHz, CD₂Cl₂) δ = 15.3 (d, *J*_{PRh} = 118 Hz). ¹H NMR (500 MHz, CD₂Cl₂) δ = 8.69 (2H, dm, *J* = 8.2 Hz, ar. CH), 8.65 (2H, dm, *J* = 8.2 Hz, ar. CH), 8.55 (2H, dm, *J* = 7.9 Hz, ar. CH), 7.97-7.95 (2H, m, ar. CH), 7.93-7.91 (2H, m, ar. CH), 7.69-7.66 (2H, m, ar. CH), 7.62-7.59 (4H, m, ar. CH), 7.55-7.52 (2H, m, ar. CH), 3.21 (4H, br s, PhobP-*H*), 2.81 (4H, br m, PhobP-*H*), 2.11-1.27 (20H, br m, PhobP-*H*). **Anal.** Found (calcd for C₄₅H₄₆ClOP₂Rh · 1.5 CH₂Cl₂): C, 59.76 (60.02), H, 5.36 (5.31). **HR-MS (ESI)** *m/z* calculated for C₄₅H₄₆ClNaOP₂Rh [M + Na]⁺ = 825.1660; obs.: 825.1681. **IR** spectrum (CH₂Cl₂): 1951 cm⁻¹ ν(CO).



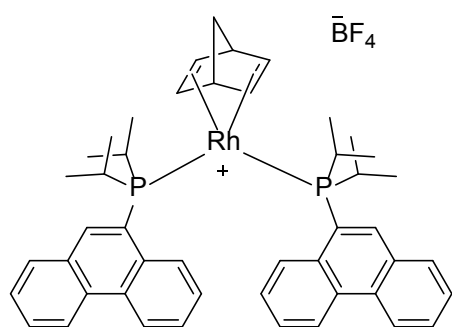
[Rh(nbd)(L_{1a})] [BF₄] (5a). A solution of **L_{1a}** (23.8 mg, 0.0806 mmol) in CH₂Cl₂ (0.4 mL) was added to a solution of [Rh(nbd)₂]BF₄ (15.1 mg, 0.0403 mmol) in CH₂Cl₂ (0.4 mL). After 5 mins, hexane (2 mL) was added to precipitate an orange solid. The supernatant was filtered off and the resulting solid washed with

hexane (2 × 0.5 mL) and dried *in vacuo* to afford **5a** as an orange powder (26.3 mg,

0.0302 mmol, 75%). $^{31}\text{P}\{^1\text{H}\}$ NMR (122 MHz, CD_2Cl_2) $\delta = -20.6$ (d, $J_{\text{PRh}} = 129$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, CD_2Cl_2) $\delta = \sim 38$ (very broad singlet, BP), -1.8 (s, BF_4^-). ^{19}F NMR (470 MHz, CD_2Cl_2) $\delta = -151.2$. ^1H NMR (500 MHz, CD_2Cl_2) $\delta = 8.60$ - 8.58 (2H, br m, ar. CH), 8.40 (2H, br s, ar. NH), 8.25 (2H, d, $J = 8.3$ Hz, ar. CH), 8.17 (2H, d, $J = 8.1$ Hz, ar. CH), 7.67 - 7.64 (2H, m, ar. CH), 7.42 - 7.39 (4H, m, ar. CH), 7.36 - 7.33 (2H, m, ar. CH), 7.25 - 7.22 (2H, m, ar. CH), 5.02 (4H, br s, alkene CH), 3.89 (2H, br s, nbd alkyl CH), 2.50 (4H, br s, $^i\text{Pr-CH}$), 1.62 (2H, s, nbd CH_2), 1.45 - 1.41 (12H, m, $^i\text{Pr-CH}_3$), 1.17 - 1.13 (12H, m, $^i\text{Pr-CH}_3$). **Anal.** Found (calcd for $\text{C}_{43}\text{H}_{54}\text{B}_3\text{F}_4\text{N}_2\text{P}_2\text{Rh}$): C, 59.56 (59.22), H, 6.49 (6.24), N, 3.25 (3.21).

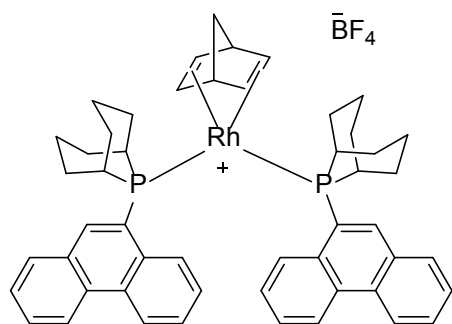


[Rh(nbd)(L_{1b})] $[\text{BF}_4]$ (5b). A solution of **L_{1b}** (23.6 mg, 0.0739 mmol) in CH_2Cl_2 (0.4 mL) was added to a solution of $[\text{Rh}(\text{nbd})_2]\text{BF}_4$ (13.8 mg, 0.0370 mmol) in CH_2Cl_2 (0.4 mL) and left to stand at RT o/n. After this time, orange crystals had precipitated out. These were filtered off, washed with CH_2Cl_2 (2×0.5 mL), and dried *in vacuo* (15.2 mg, 0.0165 mmol, 45%). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2) $\delta = -30.7$ (br d, $J_{\text{PRh}} = 130$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, CD_2Cl_2) $\delta = \sim 37$ (very broad singlet, BP), -1.6 (s, BF_4^-). ^{19}F NMR (470 MHz, CD_2Cl_2) $\delta = -148.8$. ^1H NMR (500 MHz, CD_2Cl_2) $\delta = 9.02$ (2H, br s, NH), 8.63 (2H, br s, ar. CH), 8.47 (2H, br s, ar. CH), 8.31 (2H, d, $J = 7.5$ Hz, ar. CH), 8.05 (2H, br s, ar. CH), 7.86 (2H, br s, ar. CH), 7.63 (2H, br s, ar. CH), 7.56 (2H, br s, ar. CH), 7.38 (2H, br s, ar. CH), 4.90 (2H, br s, nbd alkene CH), 4.81 (2H, br s, nbd alkene CH), 3.91 (2H, br s, nbd alkyl CH), 2.89 (2H, br s, PhobP-CH), 2.78 (2H, br s, PhobP-CH), 2.62 (2H, br s, PhobP- CH_2), 2.09 - 1.72 (14H, br m, PhobP- CH_2), 1.68 (2H, s, nbd CH_2), 1.46 - 1.08 (8H, br m, PhobP- CH_2). **Anal.** Found (calcd for $\text{C}_{47}\text{H}_{54}\text{B}_3\text{F}_4\text{N}_2\text{P}_2\text{Rh}$): C, 61.20 (61.34), H, 5.77 (5.91), N, 3.35 (3.04).



[Rh(nbd)(L_{2a})] $[\text{BF}_4]$ (6a). A solution of **L_{2a}** (42.0 mg, 0.143 mmol) in CH_2Cl_2 (1 mL) was added to a solution of $[\text{Rh}(\text{nbd})_2]\text{BF}_4$ (26.7 mg, 0.0713 mmol) in CH_2Cl_2 (1 mL). After 5 mins, hexane (4 mL) was added to precipitate an orange solid. The supernatant was filtered off and the resulting solid washed with hexane (2×1 mL) and dried *in vacuo* to afford **6a** as an orange powder (59.8 mg, 0.0687 mmol, 96%). $^{31}\text{P}\{^1\text{H}\}$ NMR (122 MHz, CH_2Cl_2) $\delta = 19.3$ (d,

$J_{\text{PRh}} = 146$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, CD_2Cl_2) $\delta = -2.0$. ^{19}F NMR (282 MHz, CD_2Cl_2) $\delta = -153.3$. ^1H NMR (300 MHz, CD_2Cl_2 , -40 °C) $\delta = 9.28$ (2H, d, $J = 8.2$ Hz, ar. CH), 8.92 (2H, d, $J = 8.3$ Hz, ar. CH), 8.83-8.80 (2H, m, ar. CH), 8.01-7.78 (10H, m, ar. CH), 6.84 (2H, d, $J = 8.2$ Hz, ar. CH), 5.42 (2H, br s, nbd alkene CH), 5.26 (2H, br s, nbd alkene CH), 4.35 (2H, br s, nbd alkyl CH), 3.08 (2H, m, $^i\text{Pr-CH}$), 1.88 (2H, br s, $^i\text{Pr-CH}$), 1.04-0.97 (8H, m, $^i\text{Pr-CH}_3$ + nbd CH_2 , tentative), 0.76-0.71 (6H, m, $^i\text{Pr-CH}_3$), 0.48-0.34 (m, 12H, $^i\text{Pr-CH}_3$). **Anal.** Found (calcd for $\text{C}_{47}\text{H}_{54}\text{BF}_4\text{P}_2\text{Rh}$): C, 65.30 (64.84), H, 6.35 (6.25). **HR-MS (ESI)** m/z calculated for $\text{C}_{47}\text{H}_{54}\text{P}_2\text{Rh} [\text{M}]^+ = 783.2750$; obs.: 783.2747.



[Rh(nbd)(L_{2b})]⁺[BF₄⁻] (6b). A solution of L_{2b} (55.0 mg, 0.173 mmol) in CH_2Cl_2 (1 mL) was added to a solution of $[\text{Rh}(\text{nbd})_2]\text{BF}_4$ (32.3 mg, 0.0864 mmol) in CH_2Cl_2 (1 mL). After 10 min, the ^{31}P NMR spectrum showed the desired product (82%) as well as a doublet at 27.9 ppm ($J = 219$ Hz, 18%). After one hour stirring at 40 °C or overnight at RT, the solution turned from a pale orange to a dark red and the ^{31}P NMR spectrum showed complete conversion to the product. The solution was filtered through silica and the volatiles removed *in vacuo*. Washing the product with toluene (2×1 mL) and hexane (1 mL) and drying *in vacuo* gave the product as an orange powder (27.9 mg, 0.0304 mmol, 35%). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) $\delta = -2.0$ (d, $J_{\text{PRh}} = 152$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CD_2Cl_2) $\delta = -2.0$. ^{19}F NMR (377 MHz, CD_2Cl_2) $\delta = -153.3$. ^1H NMR (400 MHz, CD_2Cl_2) $\delta = 9.58$ (2H, br d, $J = 8.2$ Hz, ar. CH), 8.91 (2H, br d, $J = 8.3$ Hz, ar. CH), 8.84 (2H, br d, $J \approx 8$ Hz, ar. CH), 8.19 (2H, dm, $J = 7.1$ Hz, ar. CH), 8.04-8.00 (2H, m, ar. CH), 7.96-7.89 (6H, m, ar. CH), 7.51 (2H, d, $J = 9.1$ Hz, ar. CH), 5.29 (2H, br s, nbd alkene CH), 5.26 (2H, br s, nbd alkene CH), 4.35 (2H, br s, nbd alkyl CH), 2.80 (2H, br s, Phob-CH), 1.92 (2H, s, nbd- CH_2), 1.90-0.51 (24H, br m, Phob- CH_2), -0.14 (2H, br s, Phob-CH). **HR-MS (ESI)** m/z calculated for $\text{C}_{51}\text{H}_{54}\text{P}_2\text{Rh} [\text{M}]^+ = 831.2750$; obs.: 831.2754. **Anal.** Found (calcd for $\text{C}_{51}\text{H}_{54}\text{BF}_4\text{P}_2\text{Rh}$): C, 66.98 (66.68), H, 5.70 (5.93).

Hydrogenation of Cyclohexene

In a typical experiment, an NMR tube fitted with a J-Young's tap was charged with cyclohexene (10 mg, 0.12 mmol), the catalyst **5a**, **5b**, **6a** or **6b** (6.1 μmol) and 0.6 mL CD_2Cl_2 (0.6 mL). The solution was pressurised with H_2 (2 bar) and the cyclohexene conversion was monitored by ^1H NMR spectroscopy.

Crystallography

X-ray diffraction experiments on **PhobPSiMe₃**, **L_{2a}**, **L_{2b}**, **3a**, **4a** and **4b** were carried out at 100K on a Bruker APEX II diffractometer using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The X-ray diffraction experiment on **3b** was carried out at 100K on a Bruker Microstar rotating anode diffractometer using Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$). Data collections were performed using a CCD area detector from a single crystal mounted on a glass fibre. Intensities were integrated⁴ from several series of exposures measuring 0.5° in ω or ϕ . Absorption corrections were based on equivalent reflections using SADABS or TWINABS.⁵ The structures were solved using SHELXS and refined against all F_o^2 data with hydrogen atoms riding in calculated positions using SHELXL.⁶ Crystal structure and refinement data are given in Table 1.

L_{2b} crystallised as a mixture of the phosphine (45%) and the corresponding phosphine oxide (55%). **3b** has disorder over one of the phenanthrene units, with $\sim 10\%$ of the structure consisting of the conformer where the phenanthrene unit is rotated 180° around the P-B bond. **4b** crystallised with two molecules of CH₂Cl₂ in the unit cell. **PhobPSiMe₃** crystallised as a non-merohedral twin. N-H protons were located in the difference map and refined with fixed distances and assigned fixed isotropic parameters of 1.2 times that of the nitrogen.

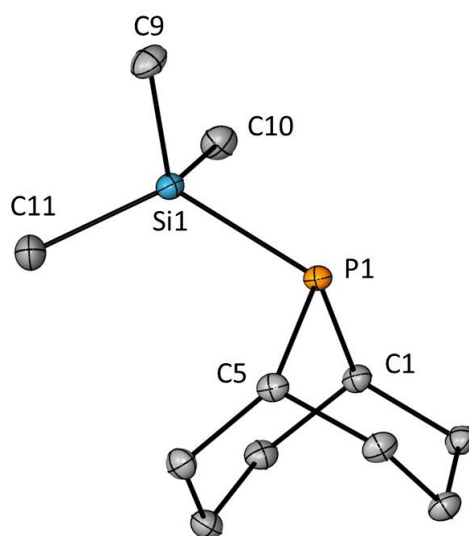


Figure S1. Thermal ellipsoid (50% probability) plot of **PhobPSiMe₃** omitting all hydrogen atoms. Selected geometrical data: bond lengths [\AA] and angles [$^\circ$]: P1-C1 1.8614(17), P1-C5 1.8660(17), P1-Si1 2.2688(9), C1-P1-C5 93.70(8), C1-P1-Si1 105.06(5), C5-P1-Si1 110.76(5).

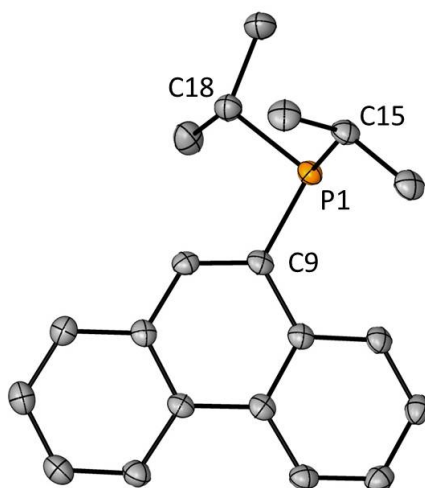


Figure S2. Thermal ellipsoid (50% probability) plot of **L_{2a}** omitting all hydrogen atoms. Selected geometrical data: bond lengths [Å] and angles [°]: C9-P1 1.8502(18), P1-C18 1.8560(19), P1-C15 1.8637(19), C18-P1-C15 103.22(9).

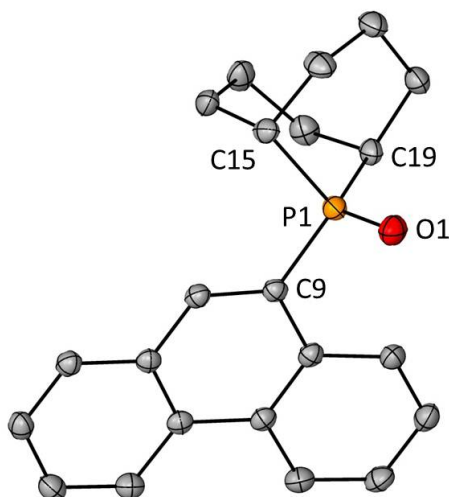


Figure S3. Thermal ellipsoid (50% probability) plot of the oxide of **L_{2b}** omitting all hydrogen atoms. Selected geometrical data: bond lengths [Å] and angles [°]: O1-P1 1.4243(18), C9-P1 1.8298(13), C19-P1 1.8365(13), C15-P1 1.8358(13), C15-P1-C19 94.90(6).

Table S1. Crystal data

| Compound | PhobPSiMe ₃ | L _{2a} | L _{2b} oxide | 3a |
|--|-------------------------------------|-----------------------------------|---|--|
| Colour, habit | colourless block | yellow plate | yellow plate | yellow block |
| Size/mm | 0.21×0.16×0.04 | 0.45×0.25×0.15 | 0.5×0.45×0.1 | 0.15×0.14×0.13 |
| Empirical Formula | C ₁₁ H ₂₃ PSi | C ₂₀ H ₂₃ P | C ₂₂ H ₂₃ O _{0.55} P | C ₃₇ H ₄₆ B ₂ ClN ₂ OP ₂ Rh |
| M | 214.35 | 294.35 | 327.19 | 756.68 |
| Crystal system | Monoclinic | Orthorhombic | Monoclinic | Monoclinic |
| Space group | <i>P2₁/c</i> | <i>Pbca</i> | <i>C2/c</i> | <i>P2₁/c</i> |
| <i>a</i> /Å | 6.581(2) | 7.1656(3) | 21.2169(10) | 9.6666(4) |
| <i>b</i> /Å | 9.426(3) | 17.6207(7) | 7.8833(4) | 23.4121(9) |
| <i>c</i> /Å | 19.551(7) | 26.1711(9) | 20.2375(10) | 8.0696(3) |
| α /° | 90.00 | 90.00 | 90.00 | 90.00 |
| β /° | 90.105(5) | 90.00 | 100.874(3) | 102.673(3) |
| γ /° | 90.00 | 90.00 | 90.00 | 90.00 |
| <i>V</i> /Å ³ | 1212.9(7) | 3304.4(2) | 3324.1(3) | 1781.78(12) |
| <i>Z</i> | 4 | 8 | 8 | 2 |
| μ /mm ⁻¹ | 0.284 | 0.158 | 0.167 | 0.677 |
| T/K | 100 | 100 | 100 | 100 |
| $\theta_{\text{min,max}}$ | 3.10,36.15 | 1.56,27.67 | 1.95,27.62 | 1.74,33.13 |
| Completeness | 0.999 to $\theta = 27.50^\circ$ | 0.993 to $\theta = 27.67^\circ$ | 0.996 to $\theta = 27.62^\circ$ | 1.000 to $\theta = 27.50^\circ$ |
| Reflections: total/independent | 5103/5103 | 96935/3834 | 56799/3864 | 58132/6399 |
| <i>R</i> _{int} | 0.0000 | 0.0931 | 0.0348 | 0.1140 |
| Final <i>R</i> 1 and <i>wR</i> 2 | 0.0440, 0.1304 | 0.0436, 0.1344 | 0.0345, 0.0922 | 0.0424, 0.0927 |
| Largest peak, hole/eÅ ⁻³ | 0.593, -0.452 | 0.356, -0.359 | 0.380, -0.268 | 0.978, -1.057 |
| ρ_{calc} /g cm ⁻³ | 1.174 | 1.183 | 1.308 | 1.410 |
| Flack parameter | n/a | n/a | n/a | n/a |

| Compound | 3b | 4a | 4b·2CH ₂ Cl ₂ |
|--|--|--|---|
| Colour, habit | orange block | yellow block | yellow block |
| Size/mm | 0.12×0.12×0.08 | 0.1×0.08×0.07 | 0.5×0.4×0.4 |
| Empirical Formula | C ₄₁ H ₄₆ B ₂ ClN ₂ OP ₂ Rh | C ₄₁ H ₄₆ ClOP ₂ Rh | C ₄₅ H ₄₆ ClOP ₂ Rh·2CH ₂ Cl ₂ |
| M | 804.72 | 755.08 | 972.97 |
| Crystal system | Monoclinic | Monoclinic | Triclinic |
| Space group | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> 2 ₁ / <i>c</i> | <i>P</i> $\bar{1}$ |
| <i>a</i> /Å | 11.4921(15) | 9.7300(3) | 8.5503(5) |
| <i>b</i> /Å | 24.764(4) | 23.1553(8) | 11.5693(7) |
| <i>c</i> /Å | 12.7559(17) | 8.0300(3) | 11.8543(7) |
| α /° | 90.00 | 90.00 | 69.300(3) |
| β /° | 90.621(5) | 103.596(2) | 84.914(3) |
| γ /° | 90.00 | 90.00 | 72.868(3) |
| <i>V</i> /Å ³ | 3630.0(8) | 1758.47(10) | 1048.11(11) |
| <i>Z</i> | 4 | 2 | 1 |
| μ /mm ⁻¹ | 5.592 | 0.685 | 0.840 |
| T/K | 100 | 100 | 100 |
| $\theta_{\text{min,max}}$ | 3.57,66.46 | 1.76,31.92 | 1.84,27.66 |
| Completeness | 0.988 to $\theta = 66.46^\circ$ | 0.998 to $\theta = 27.50^\circ$ | 0.995 to $\theta = 27.66^\circ$ |
| Reflections: total/independent | 122197/6329 | 36613/5524 | 51229/4863 |
| <i>R</i> _{int} | 0.0551 | 0.0626 | 0.0163 |
| Final <i>R</i> 1 and <i>wR</i> 2 | 0.0257, 0.0669 | 0.0361, 0.1063 | 0.0169, 0.0454 |
| Largest peak, hole/eÅ ⁻³ | 0.535, -0.499 | 0.828, -0.820 | 0.393, -0.289 |
| ρ_{calc} /g cm ⁻³ | 1.472 | 1.426 | 1.541 |
| Flack parameter | n/a | n/a | n/a |

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