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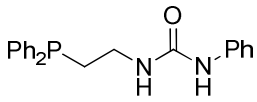
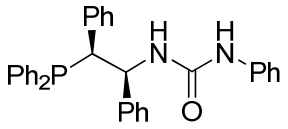
Supporting Information

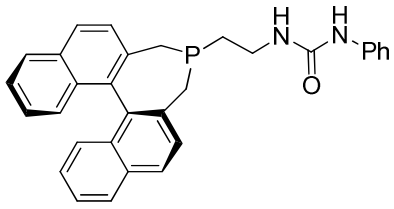
General procedure for the synthesis of ureaphosphines. 5 mmol (1 equiv) of aminophosphine was dissolved in 40 mL CH_2Cl_2. To this vigorously stirred solution was added 5.5 mmol (1.1 equiv) of isocyanate. The reaction mixture was stirred for 2 h. Solvents were evaporated *in vacuo* to provide the crude product, which was washed with hexanes (3x). Remaining solvents were evaporated *in vacuo* and the product was obtained in quantitative yield (>95% purity).



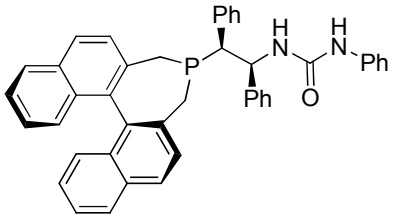
1-(2-(diphenylphosphino)ethyl)-3-phenylurea (**L1**). White powder. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.28 (t, 2H, C<u>H</u>$_2$CH$_2$NH, J = 7.2 Hz), 3.4 (m, 2H, C<u>H</u>$_2$NH), 5.4 (t, 1H, N<u>H</u>CH$_2$, J = 5.5 Hz), 6.93 (s, 1H, N<u>H</u>Ph), 7.02 (t, 1H, ArH, J = 6.9 Hz), 7.1-7.4 (m, 14H, ArH). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz) δ -20.316. ^{13}C{^{1}H} NMR ($CDCl_3$, 125.7 MHz) δ 29.248 (d, $J_{C\text{-}P}$ = 12.8 Hz, CH_2), 37.500 (d, $J_{C\text{-}P}$ = 21.5 Hz, CH_2), 120.703, 123.421, 128.600, 128.654, 128.831, 129.201, 132.695, 132.844, 137.791, 137.885, 138.849, 156.335 (NH<u>C</u>ONH). HRMS (FAB$^+$): m/z calculated for $C_{21}H_{22}ON_2P$ ([MH]$^+$): 349.1470; observed: 349.1471. Solution IR (20 mM, $CDCl_3$), ν = 3432 cm^{-1} (NH band), 1672 cm^{-1} (CO_{urea} band).



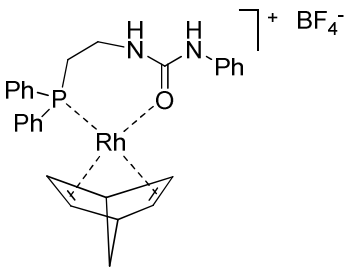
1-((1*S*,2*S*)-2-(diphenylphosphino)-1,2-diphenylethyl)-3-phenylurea (**L2**). White powder. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.17 (t, 1H, CH, J = 5.1 Hz), 5.21 (d, 1H, CH-N<u>H</u>, J = 8.4 Hz), 5.48 (m, 1H, CH), 6.27 (s, 1H, N<u>H</u>-Ph), 6.8-8.0 (m, 25H, ArH). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz) δ -9.949. ^{13}C{^{1}H} NMR ($CDCl_3$, 75.7 MHz) δ 50.931, 51.158, 56.415, 56.690, 121.103, 123.836, 126.942, 127.686, 127.913, 128.010, 128.107, 128.479, 129.223, 129.369, 129.886, 131.019, 131.132, 133.510, 133.768, 134.140, 134.415, 136.664, 136.858, 136.971, 137.084, 138.573, 139.980, 140.029, 154.765 (NH<u>C</u>ONH). HRMS (FAB$^+$): m/z calculated for $C_{33}H_{30}N_2OP$ ([MH]$^+$): 501.2096; observed: 501.2091.



1-(2-((11b*S*)-3H-dinaphtho[2,1-c:1',2'-e]phosphepin-4(5H)-yl)ethyl)-3-phenylurea (**L3**). White powder. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.38 (m, 1H, CH_2), 1.62 (m, 1H, CH_2), 2.11 (m, 1H, CH_2), 2.44 (m, 1H, CH_2), 2.51 (m, 1H, CH_2), 2.69 (m, 1H, CH_2), 3.38 (m, 2H, CH_2), 5.71 (t, 1H, N<u>H</u>CH$_2$, J = 5.4 Hz), 6.97 (t, 1H, ArH, J = 7.5 Hz), 7.2-7.6 (m, 13H, 12 ArH + 1 NHPh), 7.8-8.0 (m, 4H, ArH). ^{31}P{^{1}H} NMR ($CDCl_3$, 202.3 MHz) δ -0.518. ^{13}C{^{1}H} NMR ($CDCl_3$, 125.7 MHz) δ 27.289 (d, CH_2, $J_{C\text{-}P}$ = 18.1 Hz), 28.876 (d, CH_2, $J_{C\text{-}P}$ = 19.6 Hz), 31.856 (d, CH_2, $J_{C\text{-}P}$ = 14.6 Hz), 37.324 (d, CH_2, $J_{C\text{-}P}$ = 19.2 Hz), 120.609, 123.423, 125.048, 125.105, 126.027, 126.084, 126.669, 126.724, 127.057, 127.970, 128.046, 128.299, 128.407, 129.269, 132.176, 132.259, 132.373, 132.750, 132.944, 133.028, 133.388, 133.421, 134.841, 139.001, 156.209 (NH<u>C</u>ONH). HRMS (FAB$^+$): m/z calculated for $C_{31}H_{28}ON_2P$ ([MH]$^+$): 475.1939; observed: 475.1938.



1-((1*S*,2*S*)-2-((11b*S*)-3H-dinaphtho[2,1-c:1',2'-e]phosphepin-4(5H)-yl)-1,2-diphenylethyl)-3-phenylurea (**L4**). White powder. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.83 (s, 2H, CH_2), 2.46 (m, 1H, CH_2), 2.61 (m, 1H, CH_2), 3.11 (t, 1H, CH, J = 5 Hz), 5.63 (m, 1H, CH), 6.26 (d, 1H, NHCH, J = 8.5 Hz), 6.69 (s, 1H, NHPh), 7.0-8.0 (m, 27H, ArH). ^{31}P{^{1}H} NMR ($CDCl_3$, 202.3 MHz) δ 8.016. ^{13}C{^{1}H} NMR ($CDCl_3$, 125.7 MHz) δ 29.405 (d, CH_2, $J_{C\text{-}P}$ = 24 Hz), 30.859 (d, CH_2, $J_{C\text{-}P}$ = 15.6 Hz), 49.440 (d, CH, $J_{C\text{-}P}$ = 23.3 Hz), 57.405 (d, CH, $J_{C\text{-}P}$ = 20.2 Hz), 121.504, 124.016, 125.047, 125.188, 124.245, 126.054, 126.138, 126.950, 126.987, 127.034, 127.347, 127.703, 128.159, 128.210, 128.522, 129.502, 129.865, 126.183, 132.299, 132.585, 132.954, 133.307, 133.558, 134.908, 138.034, 138.823, 141.318, 155.622 (NHCONH). HRMS (FAB$^+$): *m/z* calculated for $C_{43}H_{36}ON_2P$ ([MH]$^+$): 627.2565; observed: 627.2577.



[Rh(**L1**-κ^2*O*,*P*)(nbd)]BF_4. To a Schlenk flask filled with equimolar amounts of **L1** and [Rh(nbd)$_2$]BF_4 was added CH_2Cl_2. After five minutes of vigorous stirring, solvents were evaporated *in vacuo*. The complex was used without further purification. Yellow powder. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.44 (s, 2H, Rh-nbd), 2.58 (t, 2H, CH_2CH_2NH, J = 10 Hz), 3.26 (s, 2H, Rh-nbd), 3.84 (m, 2H, CH_2NH), 3.92 (s, 2H, Rh-nbd), 5.35 (s, 2H, Rh-nbd), 6.68 (t, 1H, CH_2NH, J = 5.5 Hz), 7.1-7.6 (m, 15H, ArH), 7.71 (s, 1H, NHPh). ^{31}P{^{1}H} NMR ($CDCl_3$, 202.3 MHz) δ 31.4 (d, $^{1}J_{P\text{-}Rh}$ = 170 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.7 MHz) δ 29.476, 29.668, 39.066, 51.9981, 64.116, 90.512, 120.729, 124.234, 128.648, 128.813, 129.010, 129.286, 129.369, 131.435, 132.657, 132.754, 137.365, 161.506 (NHCONH). HRMS (FAB$^+$): *m/z* calculated for $C_{28}H_{29}N_2OPRh$ ([MH]$^+$): 543.1073; observed: 543.1074. Solution IR (20 mM, $CDCl_3$), ν = 1572 cm^{-1} (CO_{urea} band).

General procedure hydrogenation experiments. Substrates **S1**,[1] **S2**,[1] **S3**,[1] **S4**[2] and **S5**[3] were prepared according to published procedures. The hydrogenation experiments were carried out in an Accelerator SLT workstation of Chemspeed Technologies under inert conditions. The reaction mixtures were beforehand prepared *in situ* by addition of CH_2Cl_2 to a Schlenk flask filled with the appropriate amounts of metal precursor, ligand and substrate. The reaction mixtures were subsequently injected manually into a reaction vial of the Accelerator SLT workstation. Next, the automated program of the Accelerator SLT workstation was started, putting the reaction mixtures under an atmosphere of dihydrogen and mixing the reaction mixtures by vortex shaking. Product samples were prepared directly after completion of the program. **S1**, **S2** and **S5** were analyzed using an Interscience Trace GC Ultra (FID detector, CP-Chiralsil-DexCB column). **S3** and **S4** were analyzed using a Shimadzu 10A

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HPLC, equipped with a UV-detector (Column: Chiralpak AD, eluent: *n*-hexane:isopropyl alcohol = 90:10, flow rate: 0.6 ml.min^{-1}).

DFT calculations. The geometry optimizations were carried out with the Turbomole program[4] coupled to the PQS Baker optimizer.[5] Geometries were fully optimized at the BP86[6] level using the SV(P) basis set[7] on all atoms (small-core pseudopotential[8] on rhodium).

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